This is a digital copy of a book that was preserved for generations on library shelves before it was carefully scanned by Google as part of a project to make the world's books discoverable online.

It has survived long enough for the copyright to expire and the book to enter the public domain. A public domain book is one that was never subject to copyright or whose legal copyright term has expired. Whether a book is in the public domain may vary country to country. Public domain books are our gateways to the past, representing a wealth of history, culture and knowledge that's often difficult to discover.

Marks, notations and other marginalia present in the original volume will appear in this file - a reminder of this book's long journey from the publisher to a library and finally to you.

Usage guidelines

Google is proud to partner with libraries to digitize public domain materials and make them widely accessible. Public domain books belong to the public and we are merely their custodians. Nevertheless, this work is expensive, so in order to keep providing this resource, we have taken steps to prevent abuse by commercial parties, including placing technical restrictions on automated querying.

We also ask that you:

+ *Make non-commercial use of the files* We designed Google Book Search for use by individuals, and we request that you use these files for personal, non-commercial purposes.

+ *Refrain from automated querying* Do not send automated queries of any sort to Google's system: If you are conducting research on machine translation, optical character recognition or other areas where access to a large amount of text is helpful, please contact us. We encourage the use of public domain materials for these purposes and may be able to help.

+ *Maintain attribution* The Google "watermark" you see on each file is essential for informing people about this project and helping them find additional materials through Google Book Search. Please do not remove it.

+ *Keep it legal* Whatever your use, remember that you are responsible for ensuring that what you are doing is legal. Do not assume that just because we believe a book is in the public domain for users in the United States, that the work is also in the public domain for users in other countries. Whether a book is still in copyright varies from country to country, and we can't offer guidance on whether any specific use of any specific book is allowed. Please do not assume that a book's appearance in Google Book Search means it can be used in any manner anywhere in the world. Copyright infringement liability can be quite severe.

About Google Book Search

Google's mission is to organize the world's information and to make it universally accessible and useful. Google Book Search helps readers discover the world's books while helping authors and publishers reach new audiences. You can search through the full text of this book on the web at `http://books.google.com/`

Chem 1108.85.3 200

SIGILL : COLL : HARVARD : CANTAB : NOV : ANGL : 1650.

CHRISTO ET ECCLESIAE

BOUGHT WITH
THE INCOME FROM
THE BEQUEST OF
NATHANIEL I. BOWDITCH,
OF BOSTON,
(Class of 1822,)
26 Nov. 1890.

COMMERCIAL ORGANIC ANALYSIS

A TREATISE ON THE

PROPERTIES, PROXIMATE ANALYTICAL EXAMINATION, AND MODES OF
ASSAYING THE VARIOUS ORGANIC CHEMICALS AND PRODUCTS
EMPLOYED IN THE ARTS, MANUFACTURES, MEDICINE, &c.;

WITH CONCISE METHODS FOR

THE DETECTION AND DETERMINATION OF THEIR IMPURITIES,
ADULTERATIONS, AND PRODUCTS OF DECOMPOSITION

BY

ALFRED H. ALLEN, F.I.C., F.C.S.

PAST PRESIDENT OF THE SOCIETY OF PUBLIC ANALYSTS,
PUBLIC ANALYST FOR THE WEST RIDING OF YORKSHIRE, THE NORTHERN DIVISION OF DERBYSHIRE,
THE BOROUGH OF SHEFFIELD, &c.

Second Edition, Revised and Enlarged

VOLUME III—PART I

*ACID DERIVATIVES OF PHENOLS, AROMATIC ACIDS, TANNINS,
DYES AND COLOURING MATTERS*

LONDON
J. & A. CHURCHILL
11 NEW BURLINGTON STREET
1889

~~V.2439~~
Chem 1108.85.3

HARVARD COLLEGE
NOV 26 1890
LIBRARY

Bowditch Fund.
(III. 1.)

PREFACE TO VOLUME III.

As the manuscript of Volume III. advanced towards completion, it became evident that the subject-matter was too extensive to allow of its publication in a volume of convenient size. I therefore decided to issue it in two Parts, each of which should, to a great extent, be independent of the other.

PART I., now published, contains a Chapter on AROMATIC ACIDS, with an Appendix descriptive of the TANNINS; and a Chapter on DYES AND COLOURING MATTERS. I have found the latter subject exceptionally difficult to treat adequately, and am far from satisfied with the result. I look for some indulgence, however; for this part of the work, covering some two hundred and seventy pages, is almost entirely new, having been represented in the First Edition merely by sections on Picric Acid and Basic Aniline Derivatives.

PART II., which will complete the work, will contain Chapters on ORGANIC BASES, CYANOGEN COMPOUNDS, ALBUMINOIDS, &c., and will, if space permit, close with a General Index to all three Volumes. From past experience, I am unwilling to make any promise as to its appearance, but it will be published at as early a date as circumstances will allow.

In the Volume now issued, I have deliberately given the references to English translations or abstracts of foreign papers, as the German and other foreign periodicals, in which the descriptions of new dyes and colouring matters usually appear originally, are practically, if not absolutely, inaccessible to the great majority of English readers.

It remains for me to thank those chemists who have given me the benefit of their special experience in certain directions, and by whose assistance some of the articles have greatly profited.

ALFRED H. ALLEN.

101, Leadenhall Street,
London, E.C., *May* 1889.

CONTENTS.

ACID DERIVATIVES OF PHENOLS AND AROMATIC ACIDS.

PAGE

GENERAL CHARACTERS AND CONSTITUTION OF AROMATIC ACIDS, . 1

PHENOL-SULPHONIC ACIDS, ... 3

Sulphophenates, 7; Iodo-paraphenolsulphonic Acids, 8; Phenyl-sulphuric Acid, 9.

BENZOIC ACID, ... 10

Benzoyl series, 11; Benzoates, 16; Benzoic Aldehyde, 18; Oil of Bitter Almonds, 19; Acetophenone, 23; Hippuric Acid, 23; Benzoic Sulphinide (Saccharine), 26.

CINNAMIC ACID, ... 30

Cinnamic Ethers, 33; Aromatic Balsams, 34; Gum Benzoin, 35; Peru Balsam, Tolu Balsam, Storax, 37; Oil of Cinnamon, 45; Coumarin, 46.

PHTHALIC ACIDS, ... 47

Orthophthalic Acid, 48; Phthalic Anhydride, 49.

SALICYLIC ACID, ... 50

Hydroxybenzoic Acids, 56; Salicylates, 57; Gaultheria Oil, 58; Salol, 59; Salicylic Aldehyde, 60.

PROTOCATECHUIC ACID, ... 61

Vanillin, 62; Piperonal, 64; Catechol, 65; Guaiacol, 65.

GALLIC ACID, ... 66

Pyrogallol, 70; Pyrogallic Ethers, 72; Galleïn, 73; Cœruleïn, 73; Cœrulignone, 73; Gallocyanin, 74.

PAGE

TANNINS OR TANNIC ACIDS, ... 74

Extraction of Tannins, 75; Constitution of Tannins, 77; Action of Heat on Tannins, 78; Action of Dilute Acids on Tannins, 80; Phlobaphenes, 82; Action of fused Alkalies on Tannins, 83; Phloroglucol, 85; Varieties of Tannic Acid, 86; Catechins, 97; Kinoïn, 98; Tannin-yielding Materials, 98; Assay of Tannin Materials, 107; Tan Liquors, 125; Writing Inks, 126; Examination of Ink-marks, 129.

DYES AND COLOURING MATTERS.

CONSTITUTION OF COLOURING MATTERS, ... 131

Relations of Colouring Matters to Fibres, 134; Mordants, 135; Classification of Colouring Matters, 136.

NITRO-COLOURING MATTERS, ... 137

Picric Acid, 139; Nitrophenols, 141; Nitrophenol-sulphonic Acids, 151; Flavaurin, 151; Nitrocresols, 152; Victoria Yellow, 152; Nitronaphthols, 153; Manchester Yellow, 154; Naphthol Yellows, 156; Aurantia, 156.

NITROSO-COLOURING MATTERS, ... 157

Resorcin Green, 158; Azoresorufin, 158; Resorcin Blue, 159; Lacmoïd, 159; Naphthol Green, 160.

AURIN AND ITS ALLIES, ... 160

Rosolic Acid, 161; Corallin, 162.

PHTHALEÏNS, ... 163

Phenol-phthaleïn, 164; Fluoresceïn, 165; Chrysolin or Uranin, 166; Eosins, 169; Rhodamine, 173; Quinoline Yellow, 174; Azo-eosin, 174.

AZO-COMPOUNDS AND COLOURING MATTERS, ... 175

Azobenzene, 175; Diazobenzene Compounds, 176; Amido-azo-Compounds, 178; Aniline Yellow, Chrysoïdine, Bismarck Brown, &c., 179; Hydroxy-azo-Compounds, 181; Sulphonated Azo-Compounds, 182; Tropæolins, 183; Acid Yellow, Helianthin (methyl-orange), Diphenylamine Yellow, Azoflavine, &c., 187; Azo-Reds,

PAGE

191; Xylidine Red, 195; Tetrazo-Dyes, 196; Croceïn Scarlet, Biebrich Scarlet, &c., 196; Tetrazo-Browns, 199; Azo-Black, 200; Azo-Dyes from Benzidine, &c., 201; Chrysamine, Congo-Red, Benzopurpurin, Delta-purpurin, Benzoazurin, &c., 206; Azurine, 209; Primulin, 209; General Reactions of Azo-Dyes, 210.

ROSANILINE AND ITS ALLIES, ... 214

Rosaniline, 217; Magenta, 220; Acid Magenta, 226; Aniline Blues, 227; Aniline Violets, 233; Aniline Greens, 237; Auramine, 244; Flavaniline, 245; Phosphine, 245; Indulines and Nigrosines, 248; Aniline Black, 250.

SAFRANINES AND THEIR ALLIES, ... 252

Safranine, 256; Magdala-Red, 257; Mauveine, 257; Eurhodines, 257; Indophenols, 258; Oxazines, 259; Meldola's Blue, Muscarin, Nile Blue, 260.

COLOURING MATTERS FROM ANTHRACENE, ... 261

Anthraquinone Derivatives, 263; Alizarin, 264; Nitro-alizarin, 267; Alizarin Blue, 268; Purpurin, 270; Anthrapurpurin and Flavopurpurin, 272; Commercial Alizarin, 274; Anthraflavic Acid, 275; Reactions of Paste Colours, 276; Detection of Anthracene Dyes on the Fibre, 279; Chrysophanic Acid, 281.

SULPHURETTED AND UNCLASSIFIED COAL-TAR DYES, . . . 284

Methylene Blue, 285; Canarin, 288; Thiorubin, Curcumin, Tartrazin, Benzoflavine, 288.

COLOURING MATTERS OF NATURAL ORIGIN, ... 289

Indigo, 290; Indican, 292; Indirubin, 293; Indigotin, 294; Isatin, 295; Reduced Indigo, 296; Indigotin-sulphonic Acids, 298; Indigo Extract or Indigo-Carmine, 299; Assay of Commercial Indigo, 302; Detection of Indigo on the Fibre, 312; Chemistry of Lichens, 315; Orcinol, 318; Archil or Orchil, 320; Cudbear, 324; Litmus, 324; Indicators of Neutrality, 326; Logwood or Campeachy, 328; Brazil Wood, 333; Sandal Wood, Barwood, 335; Alkanet, 337; Safflower, 338; Quercitron, 339; Old Fustic, 343;

PAGE

Young Fustic, 345 ; Weld, 347 Yellow Berries, 348 ; Saffron, 348 ; Annatto, 351 ; Butter Colourings, 354 ; Carotin, 356 ; Turmeric, 357 ; Gamboge, 361 ; Cochineal, 363 ; Carmine, 367 ; Kermes, 369; Lac Dye, 369.

RECOGNITION OF COLOURING MATTERS, ... 371

Forms of Combination of Dyes, 372; Capillary Analysis, 375; Systematic Detection of Coal-Tar Dyes, Weingärtner's Tables, 377; Absorption-Spectra of Colouring Matters, 381; Fluorescence of Colouring Matters, 383.

EXAMINATION OF COMMERCIAL COLOURING MATTERS, ... 384

Detection of Adulterants and Impurities of Dyes, 384; Common Salt, Sodium Sulphate, Dextrin, Sugar, Starch, Arsenic, Foreign Colouring Matters, &c., 384; Miniature Dye-Tests, 388.

EXAMINATION OF DYED FIBRES, ... 389

Fastness of Dyes, 389; Recognition of Red Dyes, 390; Recognition of Dyes of Compound Shades, 392; Martinon's Tables for the Detection of Dyes on Silk, 394; Hummel's and Lepetit's Tables of Reactions of Dyes on Fibres, 398.

INDEX, ... 421

ERRATA, ... 431

ACID DERIVATIVES OF PHENOLS AND AROMATIC ACIDS.

AMONG the bodies of acid character derived from phenols, the sulphonic acids produced by the action of strong sulphuric acid on phenols occupy a prominent place. The nitro-, chloro-, and bromo-phenols also exhibit well-marked acid functions, and might be appropriately considered in the same section. Such, however, of the haloid derivatives of phenol as have any practical interest have been already described (vol. ii. page 540); while the nitro-phenols, of which picric acid is the type, will be most conveniently considered in the Chapter on "Dyes and Colouring Matters." The same remark applies to rosolic acid, the phthaleïns, and some allied bodies.

The true aromatic acids are a well-defined and important group of bodies which bear the same relation to benzene and its homologues that fatty acids bear to methane and its homologues (paraffins), and the two series of acids present many points of resemblance. Just as acetic acid may be regarded as the type of a fatty acid, so benzoic acid is representative of the aromatic acids; while a parallel to acrylic acid may be found in cinnamic acid, to lactic acid in salicylic acid, to succinic acid in phthalic acid, and so on. The following tabular arrangement renders these analogies more evident:—

Fatty Series.		Aromatic Series.	
Formic acid, .	$H.COOH$.	Benzoic acid (Phenyl-formic acid), ...	$C_6H_5 .COOH$.
Acetic acid, .	$CH_3.COOH$.	Toluic acids, ...	$C_7H_7 .COOH$.
Propionic acid, .	$C_2H_5.COOH$.	Xylic acids, ...	$C_8H_9 .COOH$.
Butyric acid, .	$C_3H_7.COOH$.	Cumic acids, ...	$C_9H_{11}.COOH$.
Acrylic acid, .	$C_2H_3.COOH$.	Cinnamic acid (Phenyl-acrylic acid), ...	$(C_6H_5)C_2H_2.COOH$.
Propiolic acid, .	$C_2H. COOH$.	Phenyl-propiolic acid, . .	$(C_6H_5)C_2.COOH$.

Fatty Series.		**Aromatic Series.**	
Succinic acid,	$C_2H_4:\left\{\begin{matrix}COOH.\\COOH.\end{matrix}\right.$	Phthalic acids, . . .	$C_6H_4:\left\{\begin{matrix}COOH.\\COOH.\end{matrix}\right.$
Glycollic acid,	$CH_2(OH).COOH.$	Salicylic acid (Hydroxybenzoic acid), . . .	$C_6H_4(OH).COOH.$
Lactic acid,	$C_2H_4(OH).COOH.$	Cresotic acids,[1] . . .	$C_7H_6(OH).COOH.$
Glyoxylic acid,	$CH(OH)_2.COOH.$	Protocatechuic acid (Dihydroxybenzoic acid),	$C_6H_3(OH)_2.COOH.$
Erythric acid,	$C_3H_4(OH)_3.COOH.$	Gallic acid (Trihydroxybenzoic acid), . . .	$C_6H_2(OH)_3.COOH.$

Many of the aromatic acids occur ready-formed, either free or combined, in resins or balsams, and in the animal organism.

All, or nearly all, the aromatic acids tabulated above are extracted by ether from their aqueous solutions. When heated with lime they split up into carbon dioxide and benzene, hydroxybenzene, or homologues or analogues thereof. Thus :—

Phthalic acid, . . $C_8H_6O_4 = CO_2 + C_7H_6O_2$, Benzoic acid.
Benzoic acid, . . $C_7H_6O_2 = CO_2 + C_6H_6$, Benzene.
Toluic acid, . . $C_8H_8O_2 = CO_2 + C_7H_8$, Toluene.
Cinnamic acid, . . $C_9H_8O_2 = CO_2 + C_8H_8$, Cinnamene.
Salicylic acid, . . $C_7H_6O_3 = CO_2 + C_6H_6O$, Phenol.
Cresotic acid, . . $C_8H_8O_3 = CO_2 + C_7H_8O$, Cresol.
Protocatechuic acid, $C_7H_6O_4 = CO_2 + C_6H_6O_2$, Catechol.
Gallic acid, . . $C_7H_6O_5 = CO_2 + C_6H_6O_3$, Pyrogallol.

The true aromatic acids, together with the phenol-sulphonic acids, are considered in detail in the following sections. In connection with each of the more important aromatic acids certain allied or derived bodies will be conveniently described. Thus hippuric acid, bitter-almond oil, and saccharine are considered in sections appended to that on benzoic acid, the aromatic balsams are described with cinnamic acid, and pyrogallol with gallic acid. The phthaleïns are not considered in connection with phthalic acid, but in a section of the chapter on "Dyes and Colouring Matters." The tannins and their derivatives will be appropriately and conveniently described in an Appendix to the chapter on the Aromatic Acids.

---

[1] Besides three isomeric cresotic acids of the formula given, $C_6H_3(CH_3):\left\{\begin{matrix}OH\\COOH,\end{matrix}\right.$ seven other acids of the same composition are known, of which mandelic or phenyl-glycollic acid, $C_6H_5.CH\left\{\begin{matrix}OH\\COOH,\end{matrix}\right.$ is the most interesting.

Among homologous acids are the following :—

$C_6H_2(CH_3)_2\left\{\begin{matrix}OH\\COOH.\end{matrix}\right.$ Hydroxymesitylenic acid.

$C_6H_4(OH).CH_2.CH_2.COOH.$ Hydrocoumaric acid.

$C_6H_5.CH_2.CH\left\{\begin{matrix}OH\\COOH\end{matrix}\right.$ Phenyl-lactic acid.

$C_6H_5.CH\left\{\begin{matrix}CH_2.OH\\COOH.\end{matrix}\right.$ Tropic or Phenyl-hydracrylic acid.

PHENOL-SULPHONIC ACIDS.

When phenol is treated with concentrated sulphuric acid it dissolves readily, with considerable rise of temperature. The product is a mixture of two isomeric phenol-sulphonic acids, $C_6H_4(OH).SO_3H$. When the phenol and acid are slowly mixed, and the liquid prevented from becoming hot, the ortho-acid is chiefly formed, but much phenol remains unattacked. By heating the mixture for some time to 100° C., the conversion of the phenol into a sulphonic acid is nearly perfect, even when but little more than the theoretical proportion of sulphuric acid has been employed, but the ortho-acid is in great part converted into para-phenolsulphonic acid, though some of the former body remains unchanged however long the heating be continued. Meta-phenolsulphonic acid ($OH : SO_3H = 1 : 3$) is not obtainable by the direct action of sulphuric acid on phenol, but may be produced by other reactions. The product of the action of sulphuric acid on phenol is frequently called sulphophenic acid or sulphocarbolic acid, and many of its salts have received application in medicine. (See page 7.)

By digesting phenol at 100° C. with a considerable excess of slightly fuming sulphuric acid, phenol-disulphonic acid, $C_6H_3(OH)(SO_3H)_2$, is produced. The solutions of this acid and its salts are coloured deep red by ferric chloride. By heating phenol under pressure with a mixture of sulphuric acid and phosphoric anhydride, a phenol-trisulphonic acid, $C_6H_2(OH)(SO_3H)_3$, is produced, crystallising in thick prisms and giving a blood-red colour with ferric chloride.

Similar series of bodies, the cresol- and xylenol-sulphonic acids, are obtained by the action of strong sulphuric acid on cresols (*Jour. Chem. Soc.*, liv. 280, 281) and xylenols respectively.

The phenol-sulphonic acids may be separated from the excess of sulphuric acid by diluting the mixture with water and digesting the solution with excess of barium carbonate. From the liquid filtered from the insoluble barium sulphate the free sulphonic acid may be prepared by precipitating the barium by an equivalent amount of dilute sulphuric acid, or the potassium or sodium salt may be obtained by precipitating the solution with a carbonate of the alkali-metal.

The following table shows the characters of the three isomeric phenol-monosulphonic acids and some of their salts:—

	Ortho-Acid. $C_6H_4\begin{cases} OH^{(1)} \\ SO_3H^{(2)} \end{cases}$.	Meta-Acid. $C_6H_4\begin{cases} OH^{(1)} \\ SO_3H^{(3)} \end{cases}$.	Para-Acid. $C_6H_4\begin{cases} OH^{(1)} \\ SO_3H^{(4)} \end{cases}$.
Free acid, .	Unknown in a pure state, being partially converted into the para-acid on evaporating the solution at 100°, and completely at a higher temperature.	Crystallises in fine needles containing 2 aqua.	Syrupy liquid, or hydrated, highly deliquescent needles.
Potassium salt,	Melts at 240°, resolidifying to a vitreous mass. Long flat needles containing 2 aq. Very soluble.	Melts at 200° to 210°. Confused efflorescent microscopic needles or scales containing 1 aq.	Melts at 400°. Anhydrous elongated hexagonal tables. Moderately soluble.
Sodium salt, .	Indistinct crystalline masses containing 1½ aq.	Flat needles or rhombic tables containing 1 aq.	Long prisms containing 2 aq.
Barium salt, .	Indistinct crystalline masses containing 2 aq. Very soluble.	Small laminæ of microscopic needles containing ½ aq. Easily soluble.	Long silky matted needles containing 3 aq.
Lead salt, .	Indistinct tables containing 1 aq. Very slightly soluble.	Large rhombic tables containing 3 aq.	Long bundles of needles containing 2 aq. Basic salt nearly insoluble.
Cupric salt, .	Pale blue prisms.	Thin bright green rhombic prisms containing 6 aq.	Deep blue plates, resembling cupric sulphate. Contains 10 aq.

When potassium ortho-phenolsulphonate is heated to 250° with caustic potash it yields catechol, or *ortho*-dihydroxybenzene, $C_6H_4(OH)^{(1)}(OH)^{(2)}$. The saltof the meta-acid when similarly treated yields *meta*-dihydroxybenzene or resorcinol, $C_6H_4(OH)^{(1)}(OH)^{(3)}$; and the para-acid probably hydroquinol, $C_6H_4(OH)^{(1)}(OH)^{(4)}$. The last body, however, is not to be found among the products of the reaction; but quinone, $C_6H_4O_2$, is produced in large quantity by treating the parasulphonate with sulphuric acid and manganese dioxide, while neither the meta- nor ortho-sulphonate yields quinone by oxidation.

The phenol-sulphonic acids are very stable bodies, and are not decomposed by boiling with caustic alkalies.

By heating the free phenol-sulphonic acids or their salts with hydrochloric or dilute sulphuric acid under pressure, they are all decomposed completely with more or less facility, phenol[1] being reproduced:—$C_6H_4(OH)SO_3K + H_2O = C_6H_5.OH + KHSO_4$.

Ortho-phenolsulphonic Acid.[2]

$$C_6H_4 \begin{cases} OH^{(1)} \\ SO_3H^{(2)}. \end{cases}$$

This body has been recently introduced as an antiseptic under the names of "aseptol" and "sozolic acid." It is prepared, mixed with more or less of the para-acid, by mixing equivalent quantities of phenol and strong sulphuric acid in the cold, and removing unacted-on sulphuric acid by adding barium carbonate. The free sulphonic acid is then obtained by treating the filtered liquid with an equivalent amount of sulphuric acid, and again filtering.

Ortho-phenolsulphonic acid is soluble in water in all proportions, and is also soluble in alcohol or glycerin. It has very little corrosive action, and is practically non-poisonous. It is alleged to have an antiseptic action three times as powerful as that of phenol, while the sodium salt is still more energetic. In its general reactions it resembles the para-acid, into which it is converted by heat.

The aseptol of commerce is a 33 per cent. aqueous solution of the phenol-sulphonic acid.

Para-phenolsulphonic Acid. Sulphophenic Acid.

$$C_6H_4 \begin{cases} OH^{(1)} \\ SO_3H^{(4)}. \end{cases}$$

This substance, also called sulphocarbolic acid, is produced commercially by the direct action of concentrated sulphuric acid on phenol. If the acids are diluted beyond a certain point no action takes place. Moderate heating and the presence of excess of sulphuric acid over the theoretical quantity are conditions facilitating the completeness of the reaction. Para-phenolsulphonic acid with some admixture of the ortho-acid results, the latter body being subsequently more or less eliminated by fractional crystallisation of the potassium salts. (See page 4.)

---

[1] The homologues of phenol, the diatomic and triatomic phenols, and other analogous bodies, also form sulphonic acids by treatment with strong sulphuric acid, the resultant compounds all being split up with formation of the original phenoloid bodies when heated with concentrated hydrochloric acid to a temperature between 100° and 200°. This general reaction is valuable, as in the form of salts of their respective sulphonic acids the various isomers and homologues may usually be separated with comparative facility by fractional crystallisation, and the phenols then regenerated by treatment with hydrochloric acid.

[2] H. E. Armstrong and some other authorities prefer, with good reason, the name phenol-orthosulphonic acid to ortho-phenolsulphonic acid. It is the sulphonic acid which is the ortho-modification, not the phenol. But as the term ortho-phenolsulphonic acid is more generally adopted, it is adhered to in the text.

Phenol is not miscible with sulphuric acid before combination, or much more soluble in dilute sulphuric acid than in water, but it is miscible in all proportions with concentrated sulphophenic acid, and in less than half its bulk of sulphophenic acid diluted with four volumes of water; addition of more water precipitates phenol, which is again dissolved on addition of sulphophenic acid. These facts are important, for they show that sulphophenic acid cannot be purified from carbolic acid by addition of water. The phenol may, however, be removed by repeatedly agitating the solution with ether free from alcohol; or the acid may be neutralised by soda, and the resultant sulphophenate crystallised from alcohol.

Para-phenolsulphonic acid may be concentrated to the condition of a syrupy liquid, and has been obtained in colourless, hydrated, extremely deliquescent needles. It is soluble in water and in alcohol, but insoluble in ether and chloroform.

Sulphophenic acid is a decided antiseptic, and its solutions coagulate albumin, but these properties are not shared by the sulphophenates until after addition of acetic acid. The free acid and its salts do not suffer decomposition in aqueous solution even when exposed to the air, and their solutions are not decomposed by boiling. The commercial *sulphocarbolates* are salts of para-phenolsulphonic acid.

Phenol-sulphonic acid and its salts are decomposed into phenol and sulphuric acid when heated with concentrated hydrochloric or dilute sulphuric acid in sealed tubes to 140° C.

A characteristic and delicate test for sulphophenic acid is to boil the liquid for a minute or two with an equal bulk of strong nitric acid, and then to neutralise the solution with potassa. A yellow colour, due to formation of potassium picrate, will be produced in a liquid containing 1 part of phenol-sulphonic acid in 50,000 of water. Carbolic acid gives the same reaction. The reaction of sulphophenic acid with nitric acid also results in the formation of sulphuric acid. Hence, if any sulphates originally present be removed by the addition of excess of barium chloride, and the solution be then boiled with nitric acid, white insoluble barium sulphate will be thrown down if a sulphophenate were present,[1] and from its weight the amount of sulphophenic acid may be calculated. ($C_6H_6SO_4 : BaSO_4 :: 173 : 233.$) The yellow liquid contains picric acid.

Another delicate though not very characteristic test for para-phenolsulphonates is the production of a deep purple colour with ferric chloride, a reaction also produced by ortho- and meta-phenolsulphonates. The colour is discharged by acids.

By the action of excess of bromine on a solution of para-phenolsulphonic acid or one of its salts, tribromo-phenol,[1] $C_6H_2Br_3.OH$, is produced, and sulphuric acid or a sulphate formed.

PARA-PHENOLSULPHONATES. SULPHOPHENATES. Sulphocarbolates.

The phenol-sulphonates are all soluble in water, and mostly soluble in alcohol, especially when hot, but are insoluble in ether. Several of them, notably the sodium and calcium salts, have been employed in medicine as a means of internally administering carbolic acid. Only distinctly crystalline specimens should be used, and they should have but a very faint odour of phenol.

The sulphophenates may be recognised by the tests for sulphophenic acid already described. The sulphophenates of the alkali-metals if ignited alone, or those of other metals if ignited with carbonate of sodium, leave a residue containing sulphate. This reaction, the formation of sulphate by boiling with nitric acid, and non-extraction by ether from acidulated solutions are characters which distinguish the sulphophenates from the salicylates.

The presence of unconverted *phenol* in sulphophenates may be detected by acidulating the solution with dilute sulphuric acid and agitating the liquid with ether or chloroform. The phenol left on spontaneous evaporation of the ether may be detected by its odour and by the yellow colour developed on warming with nitric acid and then neutralising with potassa. A faint yellow colour should be neglected, as it may be due to a trace of sulphophenic acid dissolved by the ether.

The barium, calcium, and lead salts of phenol-sulphonic acid are more or less soluble. Hence sulphuric acid and *sulphates* may be readily detected and estimated by addition of barium chloride to the original solution. *Barium* and *calcium* salts may be detected in phenolsulphonates by dilute sulphuric acid and oxalate of ammonium respectively.

Sodium Phenolsulphonate, $NaSO_3.C_6H_4.OH$, is prepared by double decomposition from the barium salt. It forms transparent rhombic crystals containing 2 aq. The salt is permanent in the air, but becomes anhydrous at 100°. At a higher temperature it evolves phenol and leaves a residue of sodium sulphate and sulphite amounting to 36 per cent. of the weight of the crystallised salt.

---

[1] This reaction enables sulphophenic acid and sulphophenates to be readily detected in presence of carbolic acid.

Sulphophenate of sodium is readily soluble in water. The solution has a cooling, saline, slightly bitter taste. The probable impurities have already been indicated (page 7).

Zinc Phenolsulphonate forms transparent efflorescent prisms or plates containing 1 aq. It also occurs as a white powder. It should leave 14·58 per cent. of zinc oxide on strong ignition. The probable impurities are *sulphates, chlorides,* compounds of the *light metals,* and free *phenol.* If prepared by the B. P. process, a notable quantity of sulphate is certain to be present.[1]

Other salts of phenol-sulphonic acid are described on page 4.

IODO-PARAPHENOLSULPHURIC ACIDS.

When 1 molecule of iodine (in the form of a mixture of potassium iodate and iodide) is added gradually to 1 molecule of potassium para-phenolsulphonate dissolved in excess of dilute hydrochloric acid, iodine at first separates, but is quickly reabsorbed, and after a short time the liquid sets to a dense mass of long thin prisms of *potassium diiodo-paraphenolsulphonate,* $C_6H_2I_2(OH).SO_3K + 2H_2O$. This salt requires about 50 parts of water for solution, and when heated decomposes without melting at about 270°, with evolution of violet vapours of iodine. It yields with potash an extremely soluble basic salt, $C_6H_2I_2(OK).SO_3K$. The *sodium salt* (normal) forms a white crystalline powder containing 2 aq., and is infusible at 200° C. It is odourless, has a faintly acid taste, is soluble in 13 parts of cold water and more readily in hot, and is also soluble in alcohol. The *barium salt* is only slightly soluble in cold water, from which it crystallises in white glistening needles. The *zinc salt* forms long colourless needles, and the *copper salt* pale green monoclinic prisms.

Free *diiodo-paraphenolsulphonic acid* melts at 120°, and decomposes with liberation of iodine at 190°.

"*Sozoiodol*" is the commercial name given to certain diiodophenolsulphonates. "Easily soluble sozoiodol" is the sodium salt, while the potassium salt forms the "difficultly soluble" modification (*Pharm. Jour.,* [3], xviii. 538, 621, 1006).

In preparing sozoiodol, a certain amount of *mono*-iodo-paraphenolsulphonic acid is produced. This acid forms thick, colourless, rhombic crystals, and differs from the di-iodo-derivative in yielding readily-soluble barium and calcium salts.

---

[1] The British Pharmacopœia directs the salt to be prepared "by heating a mixture of carbolic acid and sulphuric acid, saturating the product with oxide of zinc, evaporating and crystallising." The solution of the product is stated to be "only rendered faintly turbid by chloride of barium"!

Phenyl-Sulphuric Acid. Phenyl Hydrogen Sulphate.

$$C_6H_6SO_4 = (C_6H_5)HSO_4 = SO_2\begin{cases} OH \\ O.C_6H_5. \end{cases}$$

This acid is metameric with the phenol-sulphonic acids, $C_6H_4(OH)HSO_3$. It occurs together with its homologue cresyl-sulphuric acid, $(C_7H_7)HSO_4$, as a potassium salt in the urine of the horse and other herbivora. These salts also occur in considerable quantity in human urine after taking carbolic acid, and traces are normally present. During exhibition of phenol the inorganic sulphates ordinarily present in urine are greatly reduced in amount or even wholly disappear, being converted into phenyl-sulphates. Baumann has shown that if the inorganic sulphates be first precipitated by acidulating the urine with acetic acid and warming the diluted liquid with excess of barium chloride, the filtered liquid will contain any cresyl-sulphates and phenyl-sulphates which may be present. On boiling the filtrate for one hour with hydrochloric acid these are decomposed, barium sulphate being precipitated together with resinous matter, from which impurity it may be freed by washing with hot alcohol. On subsequently distilling the liquid the distillate contains distinct traces of phenol, directly recognisable by the bromine reaction (vol. ii. page 540); and if the distillate be shaken with ether and the ethereal solution separated and cautiously evaporated, the residue gives a distinct blue coloration with ferric chloride (vol. ii. page 539). On the contrary, from the original urine no phenol can be extracted by agitation with ether, a behaviour evidently due to the fact that the phenyl-sulphates are not decomposed till the urine is heated with acid.[1]

Baumann has actually isolated potassium phenyl-sulphate from horses' urine by the following process:—The liquid is evaporated at a low temperature, the residue extracted with alcohol, and the filtered liquid concentrated to a syrup and allowed to stand in a very cold place. The crystalline plates which form are filtered off, dried, and purified by recrystallisation from strong spirit. The pearly white tables obtained consist of potassium phenyl-sulphate (*Jour. Chem. Soc.*, xxix. 726).[1]

---

[1] E. Davies has described a specimen of urine passed by a person recovering from poisoning by carbolic acid (*Pharm. Jour.*, [3], xiv. 473). It was almost black in colour, and on distillation with sulphuric acid gave a distillate containing both phenol and cresol. The phenol was recognised by the smell, the reaction with ammonia and sodium hypochlorite, and the formation of an abundant precipitate of tribromophenol (of characteristic crystalline form) and tribromocresol on adding bromine. Only a trace of phenol distilled over when the addition of sulphuric acid was omitted, and no phenol could be extracted by ether.

Potassium Phenyl-sulphate, $(C_6H_5)KSO_4$, may also be prepared by the action of potassium phenate on potassium pyrosulphate:—$(C_6H_5).OK + K_2S_2O_7 = K_2SO_4 + (C_6H_5)KSO_4$. It crystallises in transparent rhombic tablets which feel greasy to the touch. It is readily soluble in water and sparingly soluble in cold absolute alcohol, but dissolves somewhat more readily in boiling alcohol. The aqueous solution exhibits a fine blue fluorescence.

Potassium phenyl-sulphate decomposes on exposure to moist air, sometimes in a few minutes, into phenol and potassium hydrogen sulphate. A similar change occurs by boiling the aqueous solution for a few hours, or warming it for a few minutes with dilute hydrochloric acid, but it is not affected by acetic acid. On the other hand, potassium phenyl-sulphate is stable in presence of alkalies, and is only gradually attacked by caustic potash at 150° C. When the solid salt is heated to 150°–160° in absence of moisture it is converted into the metameric potassium para-phenolsulphonate.

Phenyl-sulphates are readily distinguished from phenolsulphonates by the formation of phenol and a sulphate on heating the solution with hydrochloric acid. When solid potassium phenylsulphate is quickly heated to fusion, and then dissolved in water, the solution gives a ruby-red colour with ferric chloride.

Free phenyl-sulphuric acid is so unstable that its aqueous or alcoholic solution decomposes almost immediately.

BENZOIC ACID.

Phenyl-formic Acid. Benzene-carboxylic Acid.

$$C_7H_6O_2 = HC_7H_5O_2 = C_7H_5O.OH = C_6H_5.CO.OH.$$

Benzoic acid is the central member of a group of highly interesting bodies, a considerable number of which possess more or less practical interest. They all contain the radical benzoyl,

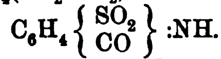
---

[1] L. Brieger treats fresh urine with neutral acetate of lead in excess, filters, and treats the filtrate with basic lead acetate. The lead is removed from the filtered liquid by sulphuretted hydrogen, and the filtrate evaporated to a thick syrup and kept some time in a vacuum. The potassium phenylsulphate forms plates which are recrystallised from hot absolute alcohol (*Jour. Chem. Soc.*, xlvi. 1353).

$C_7H_6O = C_6H_5.CO = Bz$, either intact or substituted. In the following compounds the benzoyl radical exists intact :—

Benzoic acid (Phenyl-formic acid),	$C_6H_5.CO.OH.$
Benzoyl chloride (Benzoic chloride),	$C_6H_5.CO.Cl.$
Benzoyl hydride (Benzoic aldehyde),	$C_6H_5.CO.H.$
Benzoyl methylide (Acetophenone),	$C_6H_5.CO.CH_3.$
Benzoyl-glycocine (Hippuric acid), .	$C_6H_5.CO.NH.CH_2.CO.OH.$
Benzoyl-ecgonine, ...	$C_6H_5.CO.C_9H_{14}NO_3.$
Benzoyl-methylecgonine (Cocaine), .	$C_6H_5.CO.C_9H_{13}(CH_3)NO_3.$
Benzoyl-aconine (Aconitine), . .	$C_6H_5.CO.C_{26}H_{38}NO_{11}.$

In the following allies of benzoic acid substitution occurs in the benzoyl radical itself :—

Benzoic acid (Benzene-carboxylic acid), . . .	$C_6H_5.CO.OH.$
Benzene-dicarboxylic acid (Phthalic acid)	$C_6H_4(CO.OH).CO.OH.$
Orthosulphobenzoic acid, ...	$C_6H_4(SO_2.OH).CO.OH.$
Orthosulphamidobenzoic acid, . . .	$C_6H_4(SO_2.NH_2).CO.OH.$
Benzoyl sulphonic-imide (Saccharine), . .	 $C_6H_4\left\{\begin{matrix}SO_2\\CO\end{matrix}\right\}:NH.$
Hydroxybenzoic acid (Salicylic acid), . .	$C_6H_4(OH).CO.OH.$
Dihydroxybenzoic acid (Protocatechuic acid),	$C_6H_3(OH)_2.CO.OH.$
Trihydroxybenzoic acid (Gallic acid), . .	$C_6H_2(OH)_3.CO.OH.$

Benzoic acid occurs ready-formed in gum benzoïn, storax, and Tolu and Peruvian balsams, and in these and other resins also in the form of benzoic ethers. It has also been found in the scent known as *ylang-ylang*, in vanilla, and in certain fruits, notably plums and cranberries.

Benzoic acid is formed in a number of synthetic reactions, and is produced by the oxidation of a great number of organic bodies, including benzoic and cinnamic aldehydes, toluene, cumene, casein, gelatin, &c.

The following are five of the most important and interesting methods of preparing benzoic acid :—

a. Gum Benzoïn.—The benzoic acid may be obtained by sublimation, or by exhaustion of the powdered gum with carbon disulphide. It may also be extracted from the gum by treatment with lime in the manner indicated on page 36. Benzoic acid prepared from gum benzoïn by sublimation is often more or less coloured, and has an aromatic odour.

b. Hippuric Acid, contained in the urine of herbivorous animals, splits up into benzoic acid and glycocine on putrefaction of the urine, or when boiled with hydrochloric acid (page 21).

Benzoic acid prepared from this source is apt to retain a smell of urine which can be got rid of by careful sublimation.

c. Phthalic Acid when heated with excess of slaked lime yields a mixture of calcium carbonate and benzoate ($C_8H_6O_4 = CO_2 + C_7H_6O_2$), from which benzoic acid may be readily prepared.

d. Trichlor-methylbenzene (benzenyl chloride), when heated with zinc chloride and glacial acetic acid, yields benzoic acid, acetyl chloride, and hydrochloric acid:—$C_7H_4Cl_3 + 2HC_2H_3O_2 = C_7H_6O_2 + HCl + 2C_2H_3OCl$. In order to avoid the evolution of hydrochloric acid, which carries off acetyl chloride with it, half the acetic acid may be advantageously replaced by zinc acetate. Or the formation of acetyl chloride may be avoided by heating benzenyl chloride with a little acetic acid and zinc acetate, and gradually adding the amount of water necessary for the formation of the benzoic acid.

e. Benzyl Chloride, C_7H_7Cl, (1 part) is boiled with nitric acid (3 parts of 1·31 sp. gr.) and water (2 parts) in a flask with a reflux condenser, until the odour of bitter-almonds disappears, and the liquid solidifies on cooling to a crystalline mass, free from oily drops.

Benzoic acid crystallises in lustrous scales or friable needles, but its appearance and other physical characters are greatly modified by traces of impurity, so that the impure acid has more than once been mistaken for an isomeride. When pure, benzoic acid is nearly odourless, but it frequently smells of benzoïn, and sometimes of urine or almonds. It has a sharp taste and produces a peculiar irritation in the throat. Benzoic acid has a density of 1·292, melts at 121°, and boils at 249°; but it volatilises rapidly at a temperature much below its boiling point, and forms a beautiful feathery sublimate. It is somewhat volatile in a current of steam, 1 gramme passing over with 2 litres of water, and more or less with alcohol, benzene, and other volatile liquids. The vapour of benzoic acid has a penetrating aromatic odour, attacks the eyes, and provokes coughing.

In cold water, benzoic acid dissolves very sparingly, requiring 408 parts at 15°, while at 100° the solubility is about 1 in 17. (Bourgoin, *Ann. Chim. Phys.*, [5], xv. 168.) Its solubility is greatly increased by the presence of certain salts, notably sodium phosphate.[1] It dissolves very readily in alcohol, ether, chloroform, amylic alcohol, benzene, petroleum spirit, carbon disulphide, and fixed and volatile oils.

---

[1] SODIUM BENZENE-SULPHINATE is a compound obtained by dissolving benzoic acid in a concentrated solution of sodium sulphite. It is very soluble in water at the ordinary temperature, and the solution has been recommended as an antiseptic dressing for wounds. It is said to be more efficient than phenol, and to rank with mercuric salts and iodoform, without having the poisonous characters of the former or the disagreeable odour of the latter.

Pure benzoic acid is soluble in warm concentrated sulphuric acid without coloration, and is precipitated unchanged on dilution. By fuming sulphuric acid, or more readily by sulphuric anhydride, it is converted into a sulphonic acid. Ordinary nitric acid, even when boiling, does not affect it, but it yields a nitro-derivative with the fuming acid.

Benzoic acid is not acted on by chromic acid solution; but ozone in alkaline solution oxidises it to carbonic acid and water. When swallowed by mammals, benzoic acid is converted into hippuric acid (page 21), and appears in this form in the urine; but in the organism of birds it yields ornithuric acid, $C_{19}H_{20}N_2O_4$.

When distilled with excess of baryta or slaked lime, benzoic acid is decomposed into benzene and carbon dioxide, and when its vapour is passed over faintly ignited zinc-dust it is reduced to benzoic aldehyde, C_7H_6O.

Benzoic acid is employed in medicine and the manufacture of colouring matters. It possesses decided antiseptic properties, being in this respect, according to some observers, superior to salicylic acid, and according to others inferior.

ANALYTICAL REACTIONS OF BENZOIC ACID AND BENZOATES.

Strong solutions of soluble benzoates are precipitated on addition of hydrochloric acid, owing to the slight solubility of benzoic acid in water. (Succinates give no precipitate with hydrochloric acid; but hippurates, cinnamates, and salicylates react like benzoates. Sulphuric acid should not be substituted for the hydrochloric.) The separated benzoic acid dissolves on repeated agitation with ether, chloroform, or benzene. After washing the ethereal solution with water the benzoic acid may be determined by diluting with alcohol and titrating with alkali and phenolphthaleïn. Sodium amalgam, or metallic magnesium or aluminium, gradually reduces a slightly acidified solution of a benzoate, with production of the characteristic odour of benzoic aldehyde.

Neutral ferric chloride precipitates neutral benzoates almost completely as a light red, bulky, basic ferric benzoate, insoluble in acetic acid. Succinates give with ferric chloride a reddish-brown, cinnamates a yellow, and hippurates a cream-coloured precipitate, meconates a deep red coloration, and salicylates a violet coloration. Benzoic acid is also distinguished from succinic and many other acids by not being precipitated by ammoniacal chloride of barium in presence of alcohol. Magnesium benzoate is soluble in alcohol, but the succinate is insoluble.

Benzoic acid may be *separated* from fixed substances by sublimation, and may be determined in gum benzoïn by that means.

Benzoic acid may also be approximately estimated, in the absence of interfering substances, by converting it into a soluble neutral benzoate, and precipitating the cold solution with lead acetate, avoiding excess. The precipitate is filtered off, washed once with cold water, then with proof-spirit containing ½ per cent. of acetic acid, and finally dried at 100° and weighed. Its weight, multiplied by ·5434, gives the amount of benzoic acid present.

Neutral benzoates are precipitated tolerably perfectly by cupric acetate or sulphate, and the reaction may be employed for the determination of benzoic acid.

COMMERCIAL BENZOIC ACID.

The benzoic acid of commerce is liable to contain various impurities, some of which are due to its mode of preparation, while others are intentionally added as adulterants. Asbestos, boric acid, calcium carbonate and sulphate, sal-ammoniac and sugar belong to the latter class.

Pure benzoic acid does not melt under boiling water, but certain impurities impart this property to it, besides giving it greater solubility, and causing it to form smaller crystals of a different form from that usually assumed by the pure acid. On treating a sample of benzoic acid with ether, nearly all impurities and adulterants are left undissolved, except cinnamic acid, chlorobenzoic acid, and essential oil.

Fixed impurities in benzoic acid can be detected and estimated by subliming the sample, pure benzoic acid being readily and entirely volatile. If the residue chars on further heating, *sugar* or *hippuric acid* may be present. The former gives a smell resembling burnt bread, and the latter an odour of burnt feathers, and they are readily distinguished in other ways.

The reduction of permanganate of potassium has been proposed as a test for the origin of benzoic acid, but its indications have been proved to be fallacious. Ammonio-nitrate of silver has also been recommended, the test being used at a boiling heat. Jacobsen recognises the acid from gum benzoïn by the presence of *catechol*, which he detects by converting the acid into a sodium salt, drying, and shaking with ether. The ether being separated and evaporated, the residue is dissolved and the catechol recognised by its reducing action on cold ammonio-nitrate of silver and other reactions.

Inorganic impurities will be left as a residue on igniting the sample of benzoic acid. *Chalk* dissolves readily with effervescence in dilute hydrochloric acid. *Gypsum* dissolves with difficulty, and the solution gives a white precipitate with barium chloride. *Asbestos, clay*, &c., are insoluble in dilute hydrochloric acid.

Boric acid differs from the foregoing adulterants by dissolving in hot alcohol to form a solution which when kindled burns with a flame green at the edges. (If this indication be obtained it should be confirmed by repetition on the residue left on dissolving the sample in ether, as chlorobenzoic acid might also give rise to a green-edged flame.)

Hippuric acid when present may be detected by the charring and smell of burnt feathers on heating the sample; by its incomplete solubility in ether; by its charring when heated with strong sulphuric acid; and by the evolution of ammonia which occurs when the sample is ignited with soda-lime. The last reaction may be employed quantitatively in the absence of ammoniacal salts. The proportion of hippuric acid may be approximately determined by agitating the sample with dilute hydrochloric acid and petroleum ether or chloroform, when the benzoic acid dissolves; but any hippuric (or succinic) acid remains. Samples of benzoic acid containing hippuric acid usually have a urinous odour, and redden or char when heated.

Salicylic acid may be detected by the production of a violet coloration with excess of ferric chloride.

Cinnamic acid is said to be often present in considerable proportion in the acid prepared from benzoïn. It is best detected by its reaction with manganous salts (see page 32), and by the smell of bitter-almond oil produced on warming the sample with sulphuric acid and potassium bichromate. Cinnamic acid lowers the melting point of benzoic acid (page 32).

Chlorinated compounds may be detected by dissolving the sample in alcohol, moistening some asbestos with the solution, igniting it, and placing a beaker moistened with silver nitrate over the flame. If chlorinated products were present, a milky deposit of silver chloride will be produced.

Sugar is recognised by its insolubility in ether, ready solubility in cold water, and by the blackening which occurs when the sample is heated with strong sulphuric acid. When present in quantity it may be detected by the taste of the sample, and in smaller quantity by the taste of the residue left undissolved by ether or chloroform.

Sal-ammoniac is readily detected by shaking the sample with cold water, when a solution is obtained which, on addition of argentic nitrate, gives white curdy chloride of silver insoluble in nitric acid. This proves the presence of a chloride only; the presumption that sal-ammoniac is present is confirmed if the sample evolves ammonia on treatment *in the cold* with caustic alkali. In presence of sal-ammoniac and other ammoniacal salts, the soda-lime test for hippuric acid is inapplicable, unless the sample be first shaken with cold, moderately concentrated hydrochloric acid, in which ammonium chloride dissolves, while hippuric acid is nearly insoluble.

Essential oil, which is very commonly present in the acid made from gum benzoïn, causes the sample to turn brown when warmed with strong sulphuric acid. *Resinous* and *oily matters* may also be detected by dissolving the sample in warm solution of soda, in quantity just sufficient for its neutralisation, when such impurities will remain undissolved, together with any chalk, asbestos, &c.[1]

The *odour* of benzoic acid to some extent indicates its origin from urine, &c.; but the acid from benzoïn is sometimes imitated by mixing the product from other sources with gum benzoïn, and subliming the mixture; or by adding vanillin to artificial benzoic acid. According to Hager, this factitious product may be detected by a mixture of solutions of ferric chloride and potassium ferricyanide. With the natural acid from benzoïn, the colour of this reagent is changed from yellow to blue in from 1 to 3 seconds; while with the product obtained by subliming the artificial acid over resin, from 20 seconds to 2 minutes are required.

Traces of *sulphuric* and *hydrochloric acids* are frequently present in benzoic acid, owing to the mode of preparation.

All the principal Pharmacopœias require that medicinal benzoic acid shall be prepared from gum benzoïn.

Metallic Benzoates.

The metallic benzoates are mostly crystallisable and soluble in water and alcohol, but insoluble in ether. Some of them, such as the sodium and barium salts, are withdrawn from their solutions by animal charcoal, and calcium benzoate is decomposed by it, so that free benzoic acid can be extracted by ether.

---

[1] O. Jacobsen (*Jour. Chem. Soc.*, xlvi. 1168) has recently investigated the nature of the substances accompanying benzoic acid prepared from gum benzoïn. On treating such acid with solution of sodium carbonate, an oil remains undissolved, smelling of vanillin and of phenol. This may be separated by distillation into three fractions. The first boiling between 200° and 210° consists of methyl benzoate and guaiacol, which can be separated by cold dilute caustic soda. The second and smaller fraction (boiling between 235° and 245°) when shaken with water yields up catechol, while acetyl-guaiacol remains undissolved. The third and largest fraction (boiling between 280° and 330° C.) contains benzyl benzoate, benzophenone, and benzoyl-guaiacol, with traces of vanillin and other bodies. On saponification with alcoholic potash, and agitation with water and ether, benzyl alcohol and benzophenone pass into the ethereal layer, while the alkaline solution contains benzoic acid and guaiacol.

Benzoic acid decomposes carbonates in aqueous solution, but when a current of carbon dioxide is passed through an alcoholic solution of potassium benzoate, potassium carbonate separates out.

Commercial benzoates are liable to contain much the same impurities as benzoic acid (page 14), especially *hippuric* and *chlorobenzoic acids*, *sulphates*, and *chlorides*. The two former impurities may be detected by acidulating the solution of the benzoate with hydrochloric acid and agitating with ether. Benzoic and chlorobenzoic acids pass into the ethereal layer, while hippuric acid remains undissolved in the aqueous liquid. The chlorobenzoic acid may then be detected by allowing the bulk of the ether to evaporate spontaneously, adding alcohol, igniting, and testing the products of combustion for hydrochloric acid, as described above.

Sodium Benzoate, $NaC_7H_5O_2 + 1$ aq., crystallises in colourless needles. The salt is soluble in 1·7 parts of water at 15° C., if the acid used for its preparation were pure, but has a lower but varying solubility if chlorobenzoate or hippurate be present.

Lithium Benzoate forms a crystalline powder or small shining scales, soluble in 4 parts of cold or 25 of boiling water, and in 12 parts of cold or 10 of boiling alcohol. It is liable to contain much the same impurities as sodium benzoate (see above) and lithium citrate (vol. i. page 464).

Calcium Benzoate crystallises in granules or feathery needles, and is less soluble in hot water than in cold.

Manganous Benzoate is soluble (distinction from cinnamate).

Ferric Benzoate is obtained as a flesh-red precipitate by mixing solutions of neutral benzoates of ferric chloride. It is decomposed by washing with water into a soluble acid and insoluble basic salt.

Cupric Benzoate, $Cu(C_7H_5O_2)_2 + 2$ aq., crystallises from hot water in light blue needles or plates united in spherical masses. It is one of the most insoluble of the benzoates.

Lead Benzoate is crystalline and difficultly soluble.

Benzoic Ethers.

Ethylic Benzoate, $C_2H_5.C_7H_5O_2$, is a liquid of a pleasant aromatic smell, boiling at 212°. It is used in compounding artificial fruit essences (see vol. i. page 163), and is prepared by dissolving 3 parts of benzoic acid in 2 of nearly absolute alcohol, and passing hydrochloric acid gas to saturation. The liquid is then distilled and the distillate poured into water, the separated ether being collected, dried with calcium chloride, and rectified.

Benzyl Benzoate, $C_7H_7.C_7H_5O_2$, occurs naturally as a constituent of Peru and Tolu balsams (page 38). It has a specific gravity of 1·1227 at 19°, and solidifies in a freezing mixture to a compact mass of lustrous crystals, which melt at 21°. It boils at 323° C.

Benzoic Aldehyde. Benzaldehyde. Hydride of Benzoyl.

$C_7H_6O = C_7H_5O.H. = C_6H_5.CO.H.$

Benzoic aldehyde forms the major part of the essential oils of bitter-almonds and cherry-laurel, and is now extensively manufactured synthetically.[1]

Pure benzoic aldehyde is a thin, colourless liquid of great refractive power, and peculiar, very agreeable odour, like that of bitter-almond oil, and a burning aromatic taste. Its specific gravity is 1·0636 at 0° and 1·0504 at 15° C., and its boiling point 180°. It is soluble in about 300 parts of water,[2] and is miscible in all proportions with alcohol and ether.

Exposed to the air, benzoic aldehyde absorbs oxygen greedily, and is converted into a crystalline mass of benzoic acid, $C_7H_6O_2$.[3] It is also oxidised by boiling with chromic acid mixture, or manganese dioxide and sulphuric acid; but is only slowly attacked even by boiling nitric acid.

Heated with solid caustic alkali, benzoic aldehyde evolves hydrogen and yields a benzoate. By treatment with water and sodium amalgam, it is reduced to benzyl alcohol.[4]

Like all true aldehydes, benzoyl hydride forms crystalline compounds with the acid sulphites of the alkali-metals. The sodium compound has the formula $C_7H_5NaSO_3$. Benzoic aldehyde also responds to the other general reactions of the aromatic aldehydes (vol. i. page 164). It differs from aldehydes of the fatty series in being permanent in presence of alkalies, and in not reducing Fehling's solution. Ammonia converts it into white, crystalline hydro-benzamide,[1] $(C_6H_5.CH)_3N_2$, melting at 110°, which is resolved by acids into ammonia and benzoic aldehyde.

---

[1] Benzaldehyde is prepared on a large scale by boiling 2 parts of benzyl chloride, $C_6H_5.CH_2Cl$ (formed by the action of chlorine on hot toluene), with 3 of lead or copper nitrate and 10 of water for several hours in an apparatus furnished with a reflux condenser; the operation being conducted in an atmosphere of carbon dioxide. Half the liquid is then distilled off, and the oil separated from the aqueous distillate. The product may be purified by conversion into the acid sulphite compound. Another method consists in acting on benzidene dichloride, $C_6H_5.CHCl_2$, with water and caustic soda or milk of lime, under pressure, or with glacial acetic acid and zinc chloride.

[2] The solubility is often stated at 1 in 30, or ten times the true amount.

[3] The oxidation is much retarded by the presence of hydrocyanic acid, which consequently is sometimes added to the artificial oil.

[4] Benzyl Alcohol, $C_6H_5.CH_2.OH$, is a colourless liquid of 1·051 sp. gravity, boiling at 204°, and insoluble in water but readily soluble in alcohol and ether. Oxidising agents convert it into benzoic aldehyde and benzoic acid.

Benzoic aldehyde is used as a scent and flavouring agent; for producing benzaldehyde or malachite green; and as the starting point of several other synthetical products.

ESSENTIAL OIL OF BITTER-ALMONDS.

The natural benzoic aldehyde results from the maceration of bitter-almonds with water, with subsequent distillation. Both sweet- and bitter-almonds contain a nitrogenised body called amygdalin, which under the influence of a ferment called synaptase, present in the *bitter*-almond only, is split up into benzoic aldehyde, hydrocyanic acid, and glucose.[2] $C_{20}H_{27}NO_{11} + 2H_2O = C_7H_6O + HCN + 2C_6H_{12}O_6$.

From 160 to 200 parts of bitter-almonds are required for the production of 1 part of the oil. Crude natural oil of bitter-almonds has a density varying from 1·04 to 1·075 (never more), and contains, in addition to benzoic aldehyde, benzoic and hydrocyanic acids, benzoïn, $C_{14}H_{12}O_2$, benzimide, and benzaldehyde cyanhydrin, $C_6H_5.CH(OH).CN$,[3] the nitril corresponding to mandelic acid, $C_6H_5.CH(OH).COOH$ (*Jour. Chem. Soc.*, xxxvi. 719). On fractional distillation, hydrocyanic acid passes over first, and then tolerably pure benzoic aldehyde. Benzoïn is a solid camphor-like body, and occurs most largely in samples of oil of high density, in the preparation or purification of which a high temperature has been employed. It gives a purple colour with strong sulphuric acid. Bitter-almond oil gives a crimson coloration with strong sulphuric acid, becoming brownish on exposure to the air. If the crimson liquid be poured into water the red colour disappears, and a yellow precipitate is produced, which sometimes takes the form of globules. The usual proportion of hydrocyanic acid in crude almond-oil is from 4 to 6 per cent., but it sometimes reaches a much larger amount. Of course the presence of hydrocyanic acid renders the oil poisonous; indeed, it is several times as strong in hydrocyanic acid as the B. P. acid. Hydrocyanic acid may be removed from bitter-almond oil by agitating the sample with mercuric oxide and water, or with lime and ferrous chloride, followed in either case by distillation of the oily layer.

---

[1] All the aromatic aldehydes behave in a similar manner with ammonia, thus differing from the aldehydes of the fatty series.

[2] Flückiger states that cherry-laurel leaves which have been exposed to great cold do not yield either benzoic aldehyde or hydrocyanic acid on distillation with water, the ferment apparently being killed.

[3] O. Linde (*Pharm. Jour.*, [3], xviii. 537) believes that the action of the emulsin or synaptase of the bitter-almond is limited to the formation from amygdalin of glucose and this cyanhydrin, which latter on subsequent distillation with water is partially split up into the benzoic aldehyde and hydrocyanic acid, of which the latter is soluble in water. Hence the distilled oil consists chiefly of benzoic aldehyde with from 20 to 30 per cent. of benzaldehyde cyanhydrin which has escaped decomposition. Fileti states that cherry-laurel oil contains the same body.

According to Tilden, cherry-laurel oil consists of benzoic aldehyde, less than 2 per cent. of hydrocyanic acid, a volatile oil convertible into benzoic acid by oxidation and which is possibly benzyl alcohol, and minute quantities of an odorous resin (*Pharm. Jour.*, [3], v. 761).

COMMERCIAL OIL OF BITTER-ALMONDS often contains hydrocyanic acid, which is a natural constituent of the crude oil from almonds, and is sometimes added to the artificial oil to retard oxidation. The artificial oil is liable to contain chlorinated products. In addition, oil of bitter-almonds is liable to adulteration with alcohol and nitrobenzene.

Hydrocyanic acid may be detected in bitter-almond oil by agitating the sample with water, and applying the tests for hydrocyanic acid to the aqueous liquid. Ferric chloride and ferrous chloride or sulphate should be added, and then solution of soda. On acidulating the liquid with hydrochloric acid, a bluish-green coloration or prussian-blue precipitate will be formed if hydrocyanic acid be present. An aliquot part of the aqueous solution may be employed for the determination of the hydrocyanic acid by precipitation or titration with nitrate of silver.

A preferable method is to dissolve 1 gramme of the oil in 5 c.c. of alcohol and dilute with water to 50 c.c. Excess of ammonio-nitrate of silver is then added, and the mixture well agitated for a few minutes. The solution is then slightly acidulated with nitric acid, and the precipitated cyanide of silver collected, washed, dried, and weighed, or ignited in the air and the resultant metallic silver weighed. 5 parts of silver cyanide (nearly) or 4 of metallic silver correspond to one of hydrocyanic acid.

Chlorinated products may be detected by passing the vapour of the sample together with hydrogen through a red-hot tube, as described under "Chloroform" (vol. i. page 178), or the alcoholic solution of the sample may be inflamed, and a beaker moistened with silver nitrate solution held over the flame, when white silver chloride will be deposited.

Alcohol reduces the density of bitter-almond oil. It may be approximately determined by shaking the sample in a graduated tube with water or glycerin, and noting the reduction in volume of the oily layer.

Nitrobenzene, $C_6H_5NO_2$, is occasionally used as an adulterant of bitter-almond oil, and has even been sold as a substitute under the name of "artificial essence of bitter-almonds." Nitrobenzene has a density of 1·186, and hence is heavier than bitter-almond oil, from which it also differs in not yielding benzoic acid when a current of air is passed through it.

The following method may be employed for the detection and approximate estimation of nitrobenzene in bitter-almond oil. Introduce some clean sand or emery into a wide-mouthed flask, and then add a known weight (about 10 grammes) of the sample to be tested; next add 40 c.c. of a saturated aqueous solution of acid sulphite of sodium ($NaHSO_3$), agitate briskly for a few minutes, and then shake with ether free from alcohol. The benzoic aldehyde forms a compound with the sulphite, while any nitrobenzene dissolves in the ether. The upper layer is withdrawn by a pipette, more ether added, and the agitation repeated. The pipette being again used, the united ethereal liquids are evaporated at a gentle heat, and the residual nitrobenzene is weighed. The method is only roughly approximate. If the quantity of nitrobenzene be small, or there be any doubt as to its identity, four or five drops should be dissolved in alcohol, and heated for some time with hydrochloric acid and granulated zinc. The nascent hydrogen reduces the nitrobenzene to aniline, C_6H_7N. The liquid is filtered through wet paper, rendered alkaline with solution of soda,[1] agitated with ether, and the ethereal layer removed and shaken with water and a few drops of dilute hydrochloric acid. The ether is separated, and a dilute solution of bleaching-powder is cautiously added to the aqueous liquid, when, if nitrobenzene were originally present, a violet colour (mauve) will be developed. The process requires to be skilfully conducted. This method may be conveniently used for distinguishing bitter-almond oil from nitrobenzene, but not for detecting the latter in presence of the former; when this is required, the sulphite and ether process must be previously used for their separation.[2]

The following method for detecting and approximately determining nitrobenzene in bitter-almond oil is due to Maisch. —Dissolve 1 c.c. of the sample in 12 c.c. of absolute alcohol, and add $\frac{3}{4}$ gramme of fused caustic potash. Boil the liquid till it is reduced to about 4 c.c., and leave it to cool. If the sample be pure no crystals form, but a brown colour is slowly developed. The residual liquid is entirely soluble in water. In presence of nitrobenzene, brown crystals of azo-oxybenzene, $C_{12}H_{10}N_2O$, are formed, which are insoluble in water, and may be collected, dried by pressure, and weighed.

---

[1] When the nitrobenzene occurs in quantity, bleaching-powder may be added at once to the filtered liquid after nearly neutralising it with soda.

[2] Most other essential oils can also be separated from hydride of benzoyl by means of acid sodium sulphite and ether.

M. Boyveau states that an artificial oil of bitter-almonds is occasionally met with having a density of 1·029 to 1·030. Its odour is more acrid than that of the natural oil, as may be observed by moistening strips of paper with the oil and exposing them to the air. To distinguish the natural from the artificial product, Boyveau adds 1 c.c. of the oil to an equal measure of concentrated sulphuric acid. The two liquids are shaken together, when the *natural oil* acquires a beautiful currant-red colour, which in a few hours becomes a more intense and darker red, the mixture remaining perfectly clear. Benzoic aldehyde from the *cherry-laurel* takes immediately a dark-red tint, without first passing through the delicate currant-red shade observed with bitter-almond oil. The mixture thickens somewhat, but remains perfectly fluid and clear. The oil from *peach and apricot kernels* behaves somewhat similarly, but gives an evanescent currant-red tint changing to a very dark red. *Artificial almond-oil* first takes a red tint, and then immediately becomes brown, loses its transparency, and thickens; becoming a solid brownish mass in the course of twenty-four hours. By the loss of transparency and production of the brown colour, an admixture of 25 per cent. of the artificial oil in the natural oil of bitter-almonds is said to be recognisable.

Essence of Bitter-Almonds is the name given to a solution of one part of the commercial oil of bitter-almonds in three of rectified spirit. It is employed as a flavouring agent, for which purpose it should be quite free from hydrocyanic acid. *Almond flavour* is a solution of one part of the oil in seven of rectified spirit. The proportion of alcohol in these preparations is best determined by fractional distillation.

Bitter-Almond Water is a solution of bitter-almond oil in water. It is not a preparation of the British Pharmacopœia, but is officinal in several other countries. Its strength is uncertain, however closely the specified directions for preparation are adhered to. It always contains hydrocyanic acid, the proportion of which may be determined with silver nitrate, after adding sufficient hydrated magnesia to leave the sample slightly opalescent. The mixture should be left at rest for half an hour and then titrated with decinormal silver nitrate, using neutral potassium chromate as an indicator. The use of basic acetate of magnesium is said to be preferable to that of magnesia (Beckurts, *Jour. Soc. Chem. Ind.*, vi. 567; Linde, *Jour. Chem. Soc.*, lii. 1143). Bitter-almond water should retain its characteristic odour after the removal of all the hydrocyanic acid by the above process or by agitation with excess of silver nitrate.

Laurel Water (*Aqua lauro-cerasi*), prepared by distilling laurel leaves with water,[1] and *Cherry Water*, from wild cherries, are preparations very similar to bitter-almond water; but the latter becomes milky immediately on addition of ammonia, which is an effect not produced on laurel water till after the lapse of some time.

Acetophenone. Benzoyl Methide. Phenyl-methylketone.

$$C_8H_8O = C_6H_5.CO.CH_3.$$

This body results from the reaction of benzoyl chloride on zinc-methyl, or by distilling a mixture of benzoate and acetate of calcium.

Acetophenone crystallises in large laminæ, melting at 14° to a colourless, mobile liquid of about the density of water, boiling at 198° C. It has a very persistent odour, recalling that of bitter-almond and cherry-laurel water. It is nearly insoluble in water, soluble in 60 parts of glycerin, and very soluble in alcohol, ether, chloroform, and petroleum spirit.

Acetophenone is neutral and gives no coloration or characteristic reaction with ferric chloride, hydrochloric acid, or sulphuric acid. By oxidation with chromic acid mixture it is converted into benzoic and carbonic acids.

Acetophenone has very intense hypnotic properties, and has been introduced into medicine under the name of "hypnone" (*Pharm. Jour.*, [3], xvi. 445, 582), but the statements as to its value are conflicting.

Hippuric Acid. Benzoyl-amido-acetic acid. Benzoyl glycocine.

$$C_9H_9NO_3 = C_6H_5.CO.NH.CH_2.COOH.$$

This acid replaces uric acid in the urine of herbivorous animals, which usually contains it to the extent of about 2 per cent. It is also found in small quantity in normal human urine, about 1 gramme being excreted daily, and is formed more freely when a vegetable diet is taken. In the urine of diabetic patients it is frequently present in large proportion, and is abundant in the acid urine of persons suffering from all kinds of fevers. Hippuric acid is also found in the excrement of the lower animals, except that of birds, which contains the allied substance ornithuric acid, having the constitution of a dibenzoyl-diamidovaleric acid:[1]—

---

[1] For experiments on the production of artificial laurel water, see *Jour. Chem. Soc.*, xxxii. 241.

$$\left.\begin{array}{l} C_6H_5.CO.NH \\ C_6H_5.CO.NH \end{array}\right\} :C_4H_7.COOH.$$

When benzoic acid is taken internally, it appears in the urine as hippuric acid, and hippuric acid may be obtained artificially by heating benzoic anhydride with amido-acetic acid (glycocine) or the zinc-salt of the latter with benzoyl chloride :—

$$C_7H_5O.Cl + C_2H_2(NH_2)O.OH = C_7H_5O.O.C_2H_2(NH_2)O + HCl.$$

Toluene, cinnamic acid, quinic acid, and phenyl-propionic acid when taken internally are also excreted as hippuric acid. Substituted benzoic acids appear in the urine as substituted hippuric acids.[2]

Hippuric acid crystallises in milk-white rhombic prisms ending in two or four facets, the crystals being often grouped in clumps. It has a slightly bitter but not sour taste. It melts at 187°·5, and above 240° decomposes, with an odour of hay or fresh urine, and formation of hydrocyanic and benzoic acids and benzonitril,[3] a dark resinous or coaly mass being left.

Hippuric acid requires about 600 parts of ice-cold water for solution, but dissolves tolerably readily in hot water. It is also soluble in alcohol, especially when hot. The aqueous and alcoholic solutions have an acid reaction. Hippuric acid is but slightly soluble in cold ether, but dissolves in acetic ether, and readily in boiling amylic alcohol. In chloroform, benzene, petroleum spirit, and carbon disulphide it is practically insoluble.

When boiled for a time (half an hour) with dilute nitric, hydrochloric, or oxalic acid (or more rapidly if strong hydrochloric acid be used), hippuric acid undergoes hydrolysis, the liquid on cooling depositing benzoic acid, while a salt of glycocine (amido-acetic acid) remains in solution:—$C_9H_9NO_3+H_2O=C_7H_6O_2+C_2H_5NO_2$. Strong alkalies cause a similar change. A similar reaction takes place spontaneously in urine containing hippuric acid, under the influence of the ferments present. Hence only perfectly fresh urine will yield hippuric acid. If the urine be alkaline, as is usually the case with that of herbivorous mammals, the glycocine first produced splits up into ammonia and acetic acid:—$C_2H_5NO_2+H_2O=C_2H_4O_2+NH_3$.

---

[1] On boiling ornithuric acid with hydrochloric acid it almost immediately parts with one benzoyl group and yields benzoyl-ornithine, which on further boiling splits into benzoic acid and diamido-valeric acid or ornithine, $(NH_2)_2C_4H_7.COOH$, a base of strong alkaline reaction and caustic taste.

[2] Hippuric acid may be prepared from *fresh* cows' or horses' urine, which often contains sufficient to yield a precipitate on mere addition of excess of hydrochloric acid. If not, the urine should be boiled with milk of lime, filtered, and the filtrate neutralised, concentrated, and treated with excess of hydrochloric acid ; or the neutralised filtrate may be precipitated with ferric chloride, and the washed precipitate decomposed by hydrochloric acid. The hippuric acid is freed from colouring matter by recrystallising it from chlorine water, or treating it with bleaching powder and hydrochloric acid.

[3] BENZONITRIL, or Phenyl Cyanide, $C_6H_5.CN$, is produced in a variety of reactions, but best by heating a mixture of benzoic acid and a thiocyanate. It is an oily liquid of 1·023 specific gravity at 0°, boiling at 191°, and having an odour like that of bitter-almond oil. It dissolves in about 100 parts of water, and is miscible with alcohol and ether. Boiling alkalies convert it into benzoic acid, and nascent hydrogen into benzylamine, $C_7H_7.NH_2$.

If hippuric acid be evaporated to dryness with concentrated nitric acid, and the residue heated, an odour of nitrobenzene is evolved.

Hippuric acid decomposes carbonates, and dissolves zinc with evolution of hydrogen. Its salts are mostly soluble and crystallisable. The hippurates of silver, lead, and copper are sparingly soluble.

When ferric chloride is added to a solution of a hippurate, a cream-coloured precipitate of ferric hippurate is thrown down, which contains more or less basic salt according to the greater or less dilution of the solution. The precipitate is almost insoluble in pure water, but dissolves in free hippuric acid, in excess of ferric chloride, and in alcohol. The reaction with ferric salts may be employed for the determination of hippuric acid in urine. For this purpose, the urine is acidulated with nitric acid, heated to boiling to remove carbon dioxide, neutralised with calcium carbonate, treated with excess of lead nitrate, and then diluted to a known volume and filtered. An aliquot part of the filtrate is then heated and titrated with a solution of neutral ferric nitrate which has been standardised with pure hippuric acid. The reaction is at an end when a drop of the clear liquid gives a blue coloration with potassium ferrocyanide. The distinction between this point and the previous formation of the white ferrocyanide of lead is very sharp.

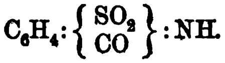
On treating ferric hippurate or the solution of a soluble hippurate with excess of hydrochloric acid, the hippuric acid separates sooner or later in long crystalline needles. These are distinguished from benzoic and salicylic acids by their crystalline form; by charring when heated with strong sulphuric acid; by giving off ammonia on ignition with soda-lime; and by not being dissolved on agitating the solution with chloroform or petroleum spirit.

For the detection of hippuric acid in the urine of the herbivora, the fresh liquid should be treated with milk of lime, filtered, the filtrate concentrated to a syrup as rapidly as possible, and excess of hydrochloric acid added, when hippuric acid crystallises out on standing. If the urine be at all putrid, benzoic acid will be obtained instead. They may be distinguished as just described.

For the detection of traces of hippuric acid in human urine, the perfectly fresh liquid should be evaporated nearly to dryness at 100°, the residue mixed with powdered sulphate of barium, a little hydrochloric acid added, and the whole exhausted with rectified spirit. The alcoholic solution is carefully neutralised with soda, and the liquid evaporated. The residue is mixed with a little oxalic acid, and again evaporated to dryness on the water-bath. The residue is exhausted with ether-alcohol, the solution distilled to a small bulk, boiled with milk of lime, filtered, concentrated, and acidulated with hydrochloric acid. Immediately or on standing, according to the quantity present, crystalline needles of hippuric acid separate, and may be filtered off and purified by washing first with diluted hydrochloric acid, and then with a little ether.

Benzoic Sulphinide. Benzoyl Sulphonic-imide.

Saccharine.



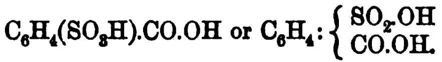
$$C_6H_4:\left\{\begin{matrix}SO_2\\CO\end{matrix}\right\}:NH.$$

The commercial product which is now becoming known by the inappropriate name of "saccharine" is quite a different body from that discovered by Peligot, and described under the name of saccharin in vol. i. page 222. The "saccharine" of Fahlberg and List is a benzoyl-sulphimide, and may be regarded as an inner anhydride of ortho-sulphamidobenzoic acid.[1] Thus:—

Benzoic acid—

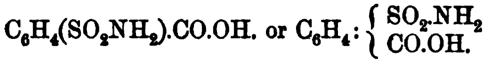
$$C_6H_5.CO.OH \text{ or } C_6H_4:\left\{\begin{matrix}H\\CO.OH.\end{matrix}\right.$$

o-Sulphobenzoic acid—



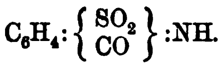
$$C_6H_4(SO_3H).CO.OH \text{ or } C_6H_4:\left\{\begin{matrix}SO_2.OH\\CO.OH.\end{matrix}\right.$$

o-Sulphamidobenzoic acid—



$$C_6H_4(SO_2NH_2).CO.OH. \text{ or } C_6H_4:\left\{\begin{matrix}SO_2.NH_2\\CO.OH.\end{matrix}\right.$$

o-Sulphamidobenzoic anhydride or Benzoic sulphinide (Saccharine)—



$$C_6H_4:\left\{\begin{matrix}SO_2\\CO\end{matrix}\right\}:NH.$$

---

[1] To obtain saccharine, toluene is first heated to 100° with concentrated sulphuric acid, whereby it is converted into a mixture of *ortho*- and *para*-toluene-sulphonic acids. The product is treated with cold water and chalk,

Saccharine forms a white powder of faintly aromatic odour, volatilising slightly at 100°, and melting at about 200° C. with partial decomposition. It crystallises from an aqueous solution in thick short prisms which are difficultly soluble in cold (1 in 1000), but more readily in boiling water (about 1 in 100). It is soluble in alcohol (1 in 80), glycerin, and moderately so in ether, and is removed from its aqueous solutions by agitation with the last solvent. It dissolves with some difficulty in chloroform and benzene, but is said to be insoluble in petroleum ether. In benzoic aldehyde it dissolves very readily.

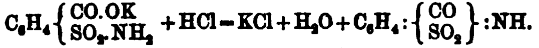
Saccharine decomposes carbonates, and forms salts, which are soluble in water, of the formula $C_6H_4(SO_2)(CO):NM$.

Saccharine is remarkable for its *intensely sweet taste*, which is probably about 130 times that of cane-sugar,[1] and is perceptible in a solution of 1 part in 10,000 of water. The sweet taste, which is associated with a faint and delicate flavour of bitter-almonds, is shared by its salts.[2] Saccharine is quite uninjurious, even when taken in considerable quantities, but passes unchanged through the system, and may afterwards be detected in the urine. It possesses moderate antiseptic properties, and now receives numerous applications as a sweetening agent under conditions where sugar would be objectionable.[3]

and the solution of the resultant calcium salts treated with sodium carbonate, the filtered liquid evaporated to dryness, and the sodium salts completely dessicated. They are then heated with phosphorus trichloride in a stream of chlorine, when *ortho-* and *para-*toluene sulphonic chlorides are formed, together with phosphorus oxychloride and sodium chloride :—

$$C_6H_4(CH_3)SO_2.ONa + PCl_3 + Cl_2 = C_6H_4(CH_3)SO_2.Cl + POCl_3 + NaCl.$$

The ortho-sulphonic chloride is liquid, and after cooling is separated from the solid crystallised para-compound by a centrifugal machine, cooled by ice to cause the last traces of the latter to crystallise. The ortho-toluenesulphonic chloride is next treated with dry ammonia gas, which converts it into ortho-toluene-sulphonic-amide, $C_6H_4(CH_3)SO_2.NH_2$, and this is separated by water from the ammonium chloride formed at the same time. By treatment with potassium permanganate and alkali, the amide is converted into a salt of ortho-sulphamidobenzoic acid, and this on treatment with a dilute mineral acid yields the corresponding anhydride, or saccharine :—



$$C_6H_4\left\{\begin{matrix}CO.OK\\ SO_2.NH_2\end{matrix}\right. + HCl = KCl + H_2O + C_6H_4:\left\{\begin{matrix}CO\\ SO_2\end{matrix}\right\}:NH.$$

[1] C. B. Allen, *Pharm. Jour.*, [3], xviii. 436. The statements made respecting the relative sweetening powers of saccharine and sugar vary very widely, ranging from 180 : 1 to 330 : 1, according to different observers.

[2] According to E. W. Gravill (*Pharm. Jour.*, [3], xviii. 837), the sweetness of the salts of saccharine is greater than that of the free acid, while the peculiar harsh taste of the latter is destroyed.

[3] Saccharine appears likely to prove especially welcome to those suffering from *diabetes*, and who consequently cannot take sugar.

An aqueous solution of saccharine gives no reaction with ferric chloride, but if previously neutralised with soda a brownish-yellow precipitate is formed.

An aqueous solution of saccharine, if not too dilute (1 in 1000), gives a characteristic apple-green coloration or precipitate when boiled with potassium ferricyanide, a slight odour of hydrocyanic acid being produced. The precipitate is soluble in caustic alkali and reproduced by hydrochloric acid (D. Sutherland).

When treated with borax in aqueous solution, saccharine is decomposed, with formation of benzoic and boric acids and sodium and ammonium sulphates (W. A. Naylor, *Pharm. Jour.*, [3], xviii. 437).

When heated with hydrochloric acid, under pressure, to 150° C., saccharine is decomposed with formation of ortho-sulphobenzoic acid and ammonium chloride.

When a solution of saccharine is evaporated with caustic alkali and the residue is heated to 250°, salicylic acid is formed, and may be detected by rendering the solution of the residue neutral or faintly acid, and adding ferric chloride, when the characteristic violet coloration will be produced.[1] On igniting a mixture of saccharine and caustic or carbonated alkali, an odour of benzene is evolved, and on dissolving the residue in water acidulated with hydrochloric acid, the solution gives a white precipitate of barium sulphate on adding barium chloride. For quantitative purposes a little nitre should be added during ignition. The saccharine represented may be found by multiplying the $BaSO_4$ found by the factor 0·785.

Börnstein has described a test for saccharine, based on the formation of a compound analogous to fluoresceïn. The saccharine is isolated by ether and the ether-residue heated in a test-tube with a slight excess of resorcinol and a drop or two of sulphuric acid. The mixture becomes yellow, red, and then dark green, and strong ebullition occurs with evolution of sulphur dioxide, which continues for a short time after the removal of the flame. The heating to ebullition is repeated once or twice, after which the mixture is allowed to cool, treated with water, and the solution supersaturated with an alkali. A reddish solution is obtained which exhibits a strong green fluorescence, perceptible with 1 part of saccharine in several millions of water. The reaction is also produced by ortho-sulphobenzoic acid.

The intensely sweet taste of saccharine and its solutions and salts is in itself highly characteristic, as is the formation of sweet vapours and sublimate on heating.[1] From sugar and other sweet substances saccharine may be separated by agitating the acidulated solution with ether. Phosphoric acid is to be preferred for acidulating the liquid. The residue obtained on evaporating the ether will have an intensely sweet taste, and will respond to the tests for saccharine already mentioned. In the case of *beer*, the bitter taste of the ethereal extract will overpower the sweet taste of any saccharine that may be present, but sulphates will be found in the residue left on igniting the ether-residue after rendering it alkaline with soda (free from sulphates).[2]

---

[1] Or the acidulated solution may be shaken with ether, the ether separated and evaporated, and the residue treated with ferric chloride.

Clause 5 of the Customs and Inland Revenue Act, 1888, enables the Commissioners to prohibit the use of saccharine in beer, at their discretion. This they have done (May 1888) till further notice.

For the detection of saccharine in *wine*, C. Schmitt recommends that 100 c.c. should be acidulated with sulphuric acid and shaken with 50 c.c. of a mixture of equal measures of ether and petroleum spirit. After separating the upper layer, and agitating the aqueous liquid with another quantity of the ethereal mixture, the ether-petroleum is evaporated with a little caustic soda solution of the residue heated to 250° and tested for salicylic acid. Of course, the absence of salicylic acid from the original wine must be first assured.

COMMERCIAL SACCHARINE is of somewhat variable quality. According to Salkowski it is liable to contain a considerable quantity of ortho-sulphobenzoic acid, and para-sulphamidobenzoic acid. The *residue on ignition* ranges from 0·6 to nearly 7·0 per cent. The ash consists chiefly of sodium sulphate, and its weight multiplied by 3 may be regarded as roughly representing the sodium sulphobenzoate and sulphamidobenzoate present. In some cases the ash has been found to contain distinct traces of iron. Sutherland has met with saccharine having a strong odour of chlorine.

Saccharine should not blacken when treated with cold concentrated sulphuric acid, and even on heating the mixture to 100° C. for ten minutes the coloration should merely be faint brown.

---

[1] D. Sutherland (*Jour. Soc. Chem. Ind.*, vi. 808) finds the microscopic appearance of the sublimate highly characteristic.

[2] The author found that if a single tablet of saccharine (containing 0·45 grain) were added to a pint of *beer*, the presence of saccharine could be readily detected by this method. That is, the beer was concentrated, acidulated with phosphoric acid (though this step was unnecessary), agitated with ether, and the residue obtained on evaporating the ether rendered alkaline with soda, ignited, and the product tested for sulphates. A blank experiment showed no trace of sulphates. The subsequent manipulation is facilitated if the beer be treated with a slight excess of lead acetate and filtered before agitating with ether. There is no occasion to remove the excess of lead; in fact, the use of sulphuretted hydrogen should be avoided (*Analyst*, xiii. 105).

If saccharine be washed on a filter with ether, and the ether agitated with ten times its measure of water, ferric chloride should not produce in it either a precipitate or a violet coloration.

The proportions of *real saccharine* present in a sample may be found by extracting the aqueous solution with ether, and evaporating the ether. A good approximation may be obtained by titrating the aqueous solution with decinormal soda and litmus or phenolphthaleïn. 1 c.c. of decinormal alkali neutralises 0·0183 gramme of saccharine.

Sugar and *glucose* will be left insoluble after repeatedly treating the solid sample with ether. A better separation can be obtained by repeatedly agitating the acidulated aqueous solution of the sample with ether. If, after removing the ether, the aqueous layer be found, after neutralisation, to have a distinctly sweet taste, the presence of sugar is certain. The quantity can be ascertained by Fehling's solution after inverting the sugar, and preferably after removing the saccharine by ether; but saccharine does not reduce Fehling's solution.

The saccharine pellets and tabloids of commerce consist in some cases of nearly pure saccharine. In others they are mixtures of saccharine with sodium bicarbonate, starch, &c.

"Dextrosaccharine" is the name given by Fahlberg to a mixture of 1 part of saccharine with from 1000 to 2000 parts of commercial glucose. The product is indistinguishable in taste from the best cane-sugar.

CINNAMIC ACID.

Phenyl-acrylic Acid.

$$C_9H_8O_2 = C_9H_8O.OH = C_6H_5.CH:CH.COOH.$$

Cinnamic acid occurs ready-formed in liquid storax, Tolu and Peruvian balsams, and in some samples of gum benzoïn; also in old oils of cinnamon and cassia, which sometimes deposit it in large prismatic crystals.

Cinnamic acid may also be prepared synthetically by a variety of reactions, including the following:—

a. By the oxidation of cinnamic aldehyde, $C_8H_8.COH$, which constitutes the greater part of the oils of cinnamon and cassia.

b. By the saponification of styracin (cinnyl cinnamate) or of cinnameïn (benzyl cinnamate):— $C_7H_7.C_9H_8O_2 + KOH = C_7H_7.OH + KC_9H_8O_2$.

c. By heating benzoic aldehyde with acetyl chloride in a sealed tube to 120°–130° C.:—$C_7H_6O + C_2H_3OCl = HCl + C_9H_8O_2$.

d. By heating benzoic aldehyde with acetic anhydride and sodium acetate : — $2C_7H_6O + C_2H_3O.O.C_2H_3O = 2C_9H_8O_2 + H_2O$. The part played by the sodium acetate is obscure.

e. By the action of sodium acetate on benzylene dichloride (prepared by the action of chlorine on toluene) :—$C_6H_5.CHCl_2 + 2CH_3.COONa = 2NaCl + C_6H_5.CH : CH.COOH + CH_3.COOH$.

The synthetical production of cinnamic acid on a large scale has recently acquired much interest as the first step in the formation of artificial indigo.

Cinnamic acid crystallises in colourless, monoclinic prisms or laminæ having a specific gravity of 1·247. It melts at 133° C., and distils with more or less decomposition at about 300°. If slowly distilled alone, or more readily if heated with lime, it splits into carbon dioxide and cinnamene, C_8H_8, a small quantity of stilbene, $C_{14}H_{12}$, being also produced.[1]

Cinnamic acid dissolves sparingly in cold water, but readily in boiling water, alcohol, and ether.

In its general properties, cinnamic acid presents a close resemblance to benzoic acid, the following being the more ready points of distinction :—

---

[1] CINNAMENE, styrolene, styrol, or phenyl-ethylene, $(C_6H_5)CH:CH_2$, exists in small quantity ready-formed in liquid storax (page 37), and may be extracted by distilling the balsam with water to which carbonate of sodium has been added to neutralise the free cinnamic acid. The hydrocarbon passes over with steam, and collects as an oil on the surface of the distillate. Cinnamene may also be obtained synthetically, and, as stated above, by heating cinnamic acid alone, or in admixture with lime or baryta. The reaction in the latter case is exactly parallel to that by which benzene is produced from benzoic acid and methane from acetic acid.

Cinnamene is a colourless, mobile liquid, having a pleasant aromatic odour. It remains fluid at −10° C. and boils at 146°, the contents of the retort being liable to rise suddenly in temperature from formation of metacinnamene.

Cinnamene resembles ethylene in its property of combining readily with chlorine, bromine, and iodine. The dibromide, $C_8H_8Br_2$, is most conveniently obtained by adding bromine to a solution of the hydrocarbon in chloroform. By oxidation, cinnamene is readily converted into benzoic acid.

Metacinnamene, $_nC_8H_8$, is formed slowly at the ordinary temperature, and readily on heating cinnamene in a sealed tube to 200°. It is a transparent, amorphous, odourless solid of high refracting power, softening on application of heat, when it may be drawn out into threads. On distillation, it is reconverted into cinnamene. Metacinnamene is insoluble in water and alcohol, and only very sparingly soluble in ether.

STILBENE, or diphenyl-ethylene, $(C_6H_5)CH.CH(C_6H_5)$, crystallises in nacreous plates, melts at 120°, and boils at about 306°. It unites with bromine to form a dibromide, $C_{14}H_{12}Br_2$, crystallising in silky needles which melt at 233°.

	Cinnamic Acid.	Benzoic Acid
Melting point, . . .	133°·3 C.	123°·3 C.
Boiling point, ...	300° C.	249° C.
Reaction in neutral solution:—		
With ferric salts, . .	Yellow.	Reddish.
With manganous salts, .	White, becoming yellow and crystalline.	No precipitate.

Cinnamic acid is also distinguished from benzoic acid by the smell of bitter-almond oil developed on warming it with chromic acid mixture. The same odour is produced by boiling cinnamic acid with water and lead dioxide, the last body gradually becoming yellow and being partially converted into benzoate of lead.

When fused at a moderate temperature with caustic potash, cinnamic acid is split up with evolution of hydrogen and formation of potassium acetate and benzoate:—$C_9H_8O_2 + 2KHO = KC_2H_3O_2 + KC_7H_5O_2 + H_2$.[1] The presence of an acetate in the product is a proof of the existence of cinnamic acid in the original substance.

Benzoic acid may be separated from cinnamic acid by crystallisation from boiling alcohol. The acids may also be separated by distillation in a current of steam, when benzoic acid nearly free from cinnamic acid passes over. By careful sublimation, the benzoic acid may also be completely separated, as little cinnamic acid volatilises below 200°.

It is probable that cinnamic acid might be determined in admixture with benzoic acid by titration with a standard solution of bromine.

J. Kachler (*Zeits. f. Chem.*, [2], vi. 59) gives the following table showing the melting points of various mixtures of cinnamic and benzoic acids. The compound 2Bz.OH + Cn.OH melts at 95° C. :—

Cinnamic Acid. Per Cent.	Benzoic Acid. Per Cent.	Melting Point. ° C.
100	0	133·3
99	1	131·8
90	10	126·6
80	20	113·0
70	30	108·2
60	40	98·7
50	50	84·3
40	60	87·1
30	70	101·4
20	80	106·4
10	90	111·5
1	99	118·2
0	100	123·3

---

[1] The change is strictly analogous to the formation of an acetate and palmitate by fusing oleic acid with caustic potash :—

$$C_{18}H_{34}O_2 + 2KHO = KC_2H_3O_2 + KC_{16}H_{31}O_2 + H_2.$$

The metallic *cinnamates* much resemble the benzoates. They are unimportant.

Cinnamic Ethers.

By the substitution of the basic hydrogen of cinnamic acid by alcohol-radicals, cinnamic ethereal salts are obtained, some of which are of importance.

ETHYL CINNAMATE, $C_2H_5.C_9H_7O_2$, is produced by distilling together cinnamic acid, alcohol, and strong sulphuric acid; or by saturating a strong alcoholic solution of cinnamic acid with hydrochloric acid gas. It is a limpid liquid of 1·30 specific gravity, boiling at 265° C. When treated with a mixture of strong nitric and sulphuric acids, avoiding rise of temperature, it is converted into a mixture of ethyl para-nitrocinnamate and ethyl ortho-nitrocinnamate. The latter body crystallises in prisms which melt at 130°, the para-compound in fine, very thin, slightly yellowish needles which melt at 138°·5 C. On heating the mixture of the two ethers with alcohol the ortho-compound only is dissolved, and is deposited on cooling in large yellowish needles. When treated with strong alkali, it is saponified with formation of ethyl alcohol and potassium ortho-nitrocinnamate, from which free orthonitrocinnamic acid, $C_9H_7(NO_2)O_2$, can be obtained by adding an acid. By treating this body with bromine it is converted into an additive compound of the formula $C_9H_7(NO_2)Br_2O_2$, which by careful treatment with caustic soda yields sodium bromide and the sodium salt of orthonitro-phenylpropiolic acid, $C_9H_5NO_4$, or $C_6H_4(NO_2).C_2.COOH$. This body, when acted on by a reducing agent, such as nascent hydrogen, glucose, or sodium xanthate, yields indigo-blue or indigotin, thus:—
$C_9H_5NO_4+H_2=C_8H_5NO+CO_2+H_2O$.

It is by the foregoing series of reactions that the production of artificial indigo on a manufacturing scale has been effected.

BENZYL CINNAMATE. Cinnameïn. $C_7H_7.C_9H_7O_2$. This body exists ready-formed in Peru and Tolu balsams. It may be obtained with some admixture of cinnyl cinnamate by treating the former substance with carbon disulphide, separating the insoluble matter, and distilling off the solvent from the solution.

Benzyl cinnamate has an agreeable taste and feeble aromatic odour, resembling that of Peruvian balsam, but without the empyreumatic smell observable in the latter. It is commonly described as an oily liquid which is liable to solidify with conversion into a crystalline isomeric body called metacinnameïn. But when obtained pure by boiling together benzyl chloride, alcohol, and dry sodium cinnamate, it forms short shining white prisms which melt at 39° C., and may remain liquid for a considerable time even if cooled to 0°. Benzyl cinnamate has a density of 1·098 in the liquid state, and distils with slight decomposition between 225° and 235°. It is nearly insoluble in water, but is readily dissolved by alcohol, ether, carbon disulphide, &c.

By long exposure to air and light, benzyl cinnamate becomes rancid and acquires an acid reaction. It is readily saponified by alcoholic potash, with formation of potassium cinnamate and benzyl alcohol, $C_7H_7.OH$.

CINNYL CINNAMATE. Styracin. $C_9H_9.C_9H_7O_2$. This body occurs together with benzyl cinnamate in liquid storax, and Peru and Tolu balsams. It crystallises in tufts of beautiful prisms, which are devoid of smell or taste and melt at 44° to a liquid which remains viscous long after cooling. It distils without decomposition in steam heated to 180°. Cinnyl cinnamate is insoluble in water and but sparingly soluble in cold alcohol or petroleum ether, but is easily soluble in ether or carbon disulphide. When treated with alcoholic potash it is saponified with formation of potassium cinnamate and

CINNYL ALCOHOL, Styryl Alcohol, or Styrone, $C_9H_9.OH$. When cinnyl cinnamate is cautiously distilled with aqueous potash, a milky distillate is obtained, and on saturating it with common salt the cinnyl alcohol forms a creamy or oily layer on the surface. It may also be extracted from the distillate or the original liquid by agitation with ether.

Cinnyl alcohol forms soft, silky needles having a sweet taste and an odour of hyacinths. It melts at 33°, and distils unchanged at 250° C. It is soluble in about 12 parts of cold water, a hot saturated solution becoming milky on cooling and remaining so for several hours, when the cinnyl alcohol separates in crystalline needles, very soluble in alcohol and ether.

Cinnyl alcohol possesses valuable antiseptic properties, being as powerful in this respect as thymol. A saturated aqueous solution forms a convenient dressing for ulcerated surfaces.

Cinnyl alcohol is converted by cautious oxidation into cinnamic aldehyde and cinnamic acid. With chromic acid mixture it becomes hot and yields cinnamic acid, which separates on the surface, and on heating this becomes further oxidised to benzoic aldehyde.

Aromatic Balsams.

The aromatic "balsams" are such of the oleo-resinous exudations of plants as contain benzoic or cinnamic acid, and yield cinnamate or benzoate of methyl or ethyl by dry distillation. The term "balsam" is misapplied to "Canada balsam" and "copaiba balsam," which are true turpentines (vol. ii. page 451), and do not contain or yield benzoic or cinnamic acid.

The aromatic balsams of practical interest are gum benzoïn, the source of the benzoic acid of pharmacy; Peruvian balsam; Tolu balsam; and liquid storax. The first of these will be conveniently considered separately, and the others conjointly under the head of "Cinnamic Balsams."

Gum Benzoïn. Gum Benjamin. Gum benzoïn is a balsamic resin obtained from *Styrax benzoïn* (and probably some allied species), a tree growing in the Malay Peninsula and Archipelago. Several varieties are known in commerce, those from Siam, Sumatra, and Penang being the chief.

Siam benzoïn is the finest variety and occurs in tears, or masses consisting of loosely agglutinated tears, of a yellow, reddish, or brown colour externally, and translucent, milk-white, or almond-like internally. It sometimes occurs in lumps of a brownish colour, which when broken present an amygdaloid appearance from the white tears imbedded in the darker coloured resinous matter. Siamese benzoïn melts at 75° C. This variety of benzoïn is never enveloped in calico.

Sumatra benzoïn has a weaker and less agreeable odour than that of Siam. It occurs in large rectangular blocks, marked with the impression of a mat and covered with a white linen cloth. When broken, few but large white tears are seen in it. It is generally composed of brown resiniform matter with numerous small white chips or pieces intermixed, which give it a granitoïd appearance. The white portions melt at 85° and the darker portions at 95° C.

Penang benzoïn closely resembles the Sumatra variety, but occasionally differs from it in colour, and more so in odour, which then suggests that of storax.

Gum benzoïn always contains more or less bark and similar matters, and in inferior specimens these are present in very large proportion. With the exception of these impurities, benzoïn should dissolve in five times its weight of alcohol. The resultant tincture from Siam benzoïn has a distinct red colour, while that yielded by the other varieties is brown or yellowish-brown. On addition of water, the liquid becomes milky, and the odour peculiar to the particular variety is readily perceived. That of Siam benzoïn is pleasantly balsamic and similar to vanilla; Penang benzoïn often smells like storax; while the odour of Sumatra benzoïn is fainter, less pleasant, and distinct from either of the former.

Gum benzoïn contains several resins, a trace of volatile oil, and from 12 to 20 per cent. of benzoic acid. Siam benzoïn also contains vanillin, and the presence of cinnamic acid has been observed in all three kinds, though the proportion varies considerably, and it is often altogether absent.[1]

The presence of cinnamic acid may be recognised by the odour of benzoic aldehyde (bitter-almond oil), developed on adding potassium permanganate to the hot liquid obtained by boiling the benzoïn with milk of lime and filtering. Or the tincture of benzoïn may be treated with water, and the liquid filtered from the precipitated resin treated with solution of permanganate or bleaching powder. Another method is to triturate the benzoïn with lead dioxide and distil the mixture with water.

The determination of the cinnamic acid may be approximately effected as indicated on page 39. As much as 11 per cent. has been found.

Gum benzoïn usually contains from 12 to 14 per cent. of benzoic acid, but occasionally 18 or 20 per cent. is reached. The proportion present may be ascertained by the following sublimation-process:—The sample is powdered, mixed with sand, and the mixture heated in a beaker or earthenware jar, furnished with a cap of filter-paper pierced with small holes. Over this is placed a cone or hood of stout paper. The benzoic acid sublimes and condenses on the inside of the hood, any oil and impurities being retained by the diaphragm of filter-paper.

Another method for the approximate assay of gum benzoïn is to digest 10 parts of the powdered gum with 6 parts of slaked lime and 100 parts of water. After six hours, the liquid is boiled, filtered, and the residue washed. The filtrate is concentrated, rendered strongly acid with hydrochloric acid, and thoroughly cooled. The precipitated benzoic acid is filtered off, washed with a little cold water, and dried between folds of blotting-paper. The small quantity of acid retained in the mother-liquor may be extracted by agitation with chloroform, and the residue left by the spontaneous evaporation of the chloroform may be added to the main quantity of benzoic acid. A preferable plan is to agitate the acidulated liquid at once with chloroform, without filtering off the precipitated benzoic acid, and to subsequently recover the benzoic acid from its chloroformic solution by the spontaneous evaporation of the solvent, assisted by a current of dry air from a bellows. If ether be substituted for the chloroform the product will contain a small quantity of water, and the determination will be too high. In any case, the benzoic acid extracted by chloroform or ether from Siamese benzoïn will be liable to contain vanillin (*Jour. Chem. Soc.*, xxxvi. 245).

---

[1] The presence of cinnamic acid, as indicated by the production of an odour of benzoic aldehyde on heating the benzoïn with chromic acid mixture, is said by Muter to be specially characteristic of the Sumatra product. He gives as specially distinctive characters of Siamese benzoïn:—The production of a cherry-red colour when sulphuric acid is added to the residue left on evaporating the solution of the gum in petroleum ether; the complete solubility of the sample in chloroform but not in ether; and the lower melting-point.

For an account of the bodies accompanying benzoic acid in benzoïn, see footnote on page 16.

Cinnamic Balsams.

Under this description are included Peruvian balsam, Tolu balsam, and liquid storax. These substances are all closely allied to one another, but in their physical properties and quantitative chemical composition, they present considerable differences.

The following table exhibits the more important distinctions between Peru and Tolu balsams and storax:—

	Peruvian Balsam.	Tolu Balsam.	Liquid Storax.
Botanical origin.	*Myroxylon*, several species.[1]	*Myroxylon.*[1]	*Styrax officinalis*; *Liquidambar orientalis.*
Geographical origin.	San Salvador, Central America.	Columbia, Turbace, Tolu, and Venezuela.	Asia Minor.
Consistency and appearance.	Viscid, but not glutinous, dark-brown liquid, resembling molasses; transparent and reddish-brown in thin layers. Gradually thickens on exposure.	When fresh, yellow, transparent, and liquid; changing rapidly to reddish-brown, and becoming solid and friable, or brittle; but softening between the teeth, and readily fusing. Such samples have a granular crystalline structure; and crystals of cinnamic acid are visible under the microscope.	Brownish-yellow or greyish, viscous liquid. Under the microscope shows globules of water, tabular crystals of cinnamic acid, and frequently feathers of styracin.
Taste.	Bitter and persistently irritating.	Sweetish, aromatic, and somewhat irritating.	Pungent and balsamic.
Odour.	Agreeable and like that of vanilla.	Aromatic, like lemon and jasmine, or suggesting vanilla; more apparent on warming.	Sweetish and resembling vanilla, or strong and oppressive.

---

[1] According to Baillon (*Pharm. Jour.*, [3], iv. 382), Peru and Tolu balsams are derived from the same tree, *Toluifera balsamum*, and the differences between the two products are due merely to differences in the mode of obtaining them.

Peruvian Balsam is readily soluble in all proportions in absolute alcohol, glacial acetic acid, chloroform, and acetone; with an equal bulk of alcohol and ether it yields a clear solution, which on further addition of the solvent becomes turbid and deposits resin. Diluted alcohol takes up only a small proportion of the balsam. Ether dissolves it.

Cold petroleum ether only dissolves the cinnameïn and cinnamic acid of the balsam, but on employing the hot solvent styracin is also dissolved, and is deposited in crystals on cooling. Carbon disulphide acts in a characteristic manner. Agitated with three times its weight of the cold solvent, the greater part of the balsam is dissolved to a colourless or slightly coloured liquid, from 10 to 16 per cent. remaining as a reddish-brown, sticky liquid, adhering firmly to the sides of the glass, while the solution may be readily poured off.

Tolu Balsam is readily soluble in alcohol, ether, chloroform, and solution of caustic potash; but benzene, petroleum ether, and carbon disulphide have little action on it, owing to the comparatively small proportion of cinnamic acid and cinnamic ethers present.[1]

Liquid Storax contains water and various impurities. With the exception of these foreign matters, it is soluble in alcohol, ether, or chloroform. With an equal weight of warm alcohol it yields a turbid solution having an acid reaction. This solution, when filtered and evaporated, yields not less than 70 per cent. of the original balsam as a brown semi-liquid residue, which constitutes the "Prepared Storax, B. P.," and is completely soluble in ether and carbon disulphide. It is soluble in benzene, but only partially soluble in cold petroleum ether. On heating it dissolves more freely, and the solution deposits crystals of cinnamic acid and styracin on cooling.

The details of the chemistry of the cinnamic balsams requires careful revision, though the main constituents of these products are satisfactorily identified. They are all closely allied to one another, consisting essentially of the benzyl and cinnyl ethers of benzoic and cinnamic acids, mixed with resinous oxidation-products of these ethers, free benzoic and cinnamic acids, and the hydrocarbon cinnamene. The leading or characteristic constituents of Peru balsam may be said to be the cinnameïn or benzyl cinnamate (page 33) and styracin or cinnyl cinnamate. Free benzyl alcohol is also present. In Tolu balsam, on the other hand, the proportion of resin is very large; but of the ethers benzyl benzoate predominates, and cinnyl benzoate and cinnamate exist in but small proportions. In liquid storax of Mexican origin, phenylpropyl cinnamate exists in considerable quantity; two isomeric alcohol-like bodies called α- and β-storesinol, to which the formula $C_{36}H_{55}.(OH)_3$ is attributed (*Ber.*, ix. 274); and the cinnamic ethers of these bodies.

---

[1] W. A. Naylor (*Pharm. Jour.*, [3], viii. 624) has described a specimen of spurious Tolu balsam sold as genuine by a large firm, which contained no cinnamic acid or cinnameïn, and was wholly soluble in carbon disulphide, chloroform, ether, and hot alcohol.

In many cases there is reason to believe that the bodies detected in the cinnamic balsams have been decomposition-products due to the methods of analysis employed. The following method may be adopted for the recognition of the principal constituents of aromatic balsams:—The substance is dissolved in two or three parts of ether, and filtered from any insoluble matter. The solution is agitated with an equal measure of normal solution of caustic soda, the alkaline liquid withdrawn, and the agitation repeated with a fresh quantity of caustic soda solution. If desired, the total acidity of the balsam can be deduced from the titration of an aliquot part of the alkaline liquid.[1] The ethereal layer is then washed with water, and distilled at a gentle heat, the residue of neutral ethers, &c., being weighed. The residue is then fractionally distilled.

The first fraction will contain any *cinnamene* which may be present, the next being rich in *benzyl alcohol*, which may be extracted by agitation with water and will yield benzoic aldehyde and acid by oxidation. *Cinnyl alcohol* and *benzyl benzoate* pass over next, and at a higher temperature *benzyl cinnamate* and *cinnyl benzoate* and *cinnamate* may be obtained. These ethers suffer more or less decomposition unless the distillation is conducted *in vacuo*, and hence the last fractions consist largely of cinnamic acid, which can be removed by agitating the distillate with sodium carbonate solution. The alkaline liquid separated from the ethereal solution should be saturated with carbonic acid, which precipitates much *resin*. The liquid is filtered, concentrated, and treated with hydrochloric acid, when a bulky precipitate is obtained representing the *free benzoic* and *cinnamic acids* of the balsam. These bodies may be identified by their ordinary reactions. For their approximate separation, one-half of the precipitate may be boiled with milk of lime and the liquid filtered and allowed to become cold, when the sparingly soluble calcium cinnamate is deposited in shining needles, the more soluble benzoate remaining in solution. The methods indicated on page 32 may also be utilised for the separation of the two acids. When an exact determination of the free acids of a balsam is desired, it is better to agitate the ethereal solution with sodium carbonate instead of with caustic soda, as the latter reagent is liable to cause some decomposition of the ethers.

---

[1] Or the sample may be dissolved in ether and the solution diluted with alcohol and titrated with standard caustic soda and phenol-phthaleïn.

Except for purposes of research, it is rarely necessary to make so full a proximate analysis of a balsam as is indicated above, but a determination of the percentage of total ethers, of free acids, and of resin is of value for judging of the genuine nature of Peruvian balsam, which is very liable to adulteration.

ADULTERATIONS OF PERUVIAN BALSAM.

Peruvian balsam is liable to adulteration with the cheaper cinnamic balsams (Tolu and storax); copaiba and gurgon balsams; colophony; an alcoholic solution or extract of gum benzoïn; alcohol; and even with fixed oils, especially castor-oil. Hence the examination of Peru balsam for the detection of these adulterants is of some importance.[1]

All the usual adulterants of Peruvian balsam have a lower specific gravity than the genuine substance, which varies in density between very narrow limits, 1·150 being the maximum and 1·137 the extreme minimum. Any sample having a lower density than 1·138 should be regarded with suspicion.

The presence of *alcohol* is indicated by the loss of volume undergone by the balsam on agitating with water. Small quantities may be detected by distilling the sample with water and sodium carbonate, and examining the distillate by the iodoform and chromic acid tests.

Much information respecting the quality and purity of a sample of balsam can be obtained by a judicious treatment with solvents. Thus, on treatment with three times its volume of carbon disulphide, Peruvian balsam dissolves to a faintly coloured solution, 16 per cent. of residue, at most, remaining as a dark sticky mass which adheres firmly to the side of the glass, allowing the solution to be poured off. Any dark coloration of the latter indicates adulteration. Petroleum dissolves Peru balsam less completely, but for this reason its indications are in many respects more reliable than those obtained with carbon disulphide. Thus cold petroleum ether dissolves the cinnameïn (benzyl cinnamate) of the sample, leaving the greater part of the styracin (cinnyl cinnamate), which in its turn can be dissolved by treating the residue with ether or hot petroleum spirit. Either of the above solvents will dissolve the free benzoic and cinnamic acid of the sample as well as the cinnameïn, and hence a more accurate determination of the latter, which may be considered the essential and characteristic constituent of Peruvian balsam, can be obtained if the free acids be first neutralised. For this purpose, the balsam should be thoroughly mixed with slaked lime and a little water, and heated on the water-bath for some hours, small quantities of water being added at intervals. The dry mixture may then be extracted with petroleum spirit.

---

[1] The following references relate to original or translated articles of recent date on the assay of the aromatic balsams:—

E. Busse, *Pharm. Jour.*, [3], vii. 354.
F. A. Flückiger, *Pharm. Jour.*, [3], xii. 45.
C. Grote, *Year-Book of Pharm.*, 1881, p. 219.
H. Hager, *Year-Book of Pharm.*, 1879, p. 257.
P. MacEwan, *Pharm. Jour.*, [3], xv. 236.
R. V. Matterson, *Year-Book of Pharm.*, 1876, p. 188.
W. A. Naylor, *Pharm. Jour.*, [3], viii. 624.
J. Peckolt, *Pharm. Jour.*, [3], xi. 819.
O. Schlickum, *Pharm. Jour.*, [3] xiii. 321.
A. Andrée, *Jour. Chem. Soc.*, l. 181.

A direct determination of the free acid of the sample will indicate an adulteration with benzoïn. For this purpose the balsam should be dissolved in ether and the solution diluted with alcohol and titrated with decinormal caustic soda, using phenolphthaleïn as an indicator. The results are conveniently expressed in terms of cinnamic acid. The presence of colophony will wholly vitiate the result of the titration.

The following table shows the densities and behaviour with solvents of Peruvian balsam and its adulterants:—

	Peru Balsam.	Purified Storax.	Alcoholic Benzoïn.	Copaiba Balsam.	Colophony.	Castor-Oil.
Specific gravity, . .	1·137 to 1·150.	1·09	1·08	·915 to ·995.	1·04 to 1·10	·960
Percentage soluble in three parts carbon disulphide, . . .	84 to 90	100	40	100	100	100
Percentage soluble in petroleum spirit (sp. gr. ·710), ...	41 to 58	33	12	100	60	variable
Percentage soluble in carbon disulphide after previous treatment, .	26 to 37	...	...	...	...	...
Percentage soluble in petroleum ether after treatment with lime and water, ...	41	35	traces	Essential oil = 25 to 65 per cent.	traces	traces
Dissolved by ether from residue from last treatment, ...	14	20	...	none	...	...

The petroleum spirit solution yielded by adulterated balsam gives on evaporation a residue which often has a characteristic odour. In the German Pharmacopœia it is stated that it should not have the odour of turpentine, storax, or copaiba, and should not give a blue or greenish-blue colour with nitric acid (sp. gr. 1·30–1·33). P. MacEwan has pointed out that the nitric acid test is vitiated unless the petroleum spirit solution be freed from suspended particles by filtration, and that the strength of the acid employed materially affects the colour obtained. He obtained the following results by allowing 1 drop of the petroleum spirit residue to fall on the surface of 10 to 20 drops of the acid contained in a porcelain dish:—

	Colour Reaction with Nitric Acid.	
	Sp. Gr. 1·42.	Sp. Gr. 1·30 to 1·33.
Pure Peruvian balsam.	Pale green, developing slowly, the margins being violet; on standing the whole becomes chocolate-brown.	The original yellow colour of the residue darkens or becomes an indistinct green.
Balsam containing storax.	Pale green, darkening to decided opaque green (without violet tint), changing to brown on standing.	Reaction the same as with pure balsam.
Balsam containing colophony.	Immediate bright emerald green.	Gradually. bright green spots on pale brown ground.
Balsam containing copaiba.	Intense blue.	Greenish-blue.

From these results it is evident that the best results are obtained by the use of the strong acid (sp. gr. 1·42).

The presence of *benzoïn* will tend to decrease the percentage soluble in carbon disulphide, while in the case of all other adulterants the proportion of soluble matter is increased. A further indication of adulteration is afforded by treating the sample with lime and water, drying, and extracting with petroleum spirit. Under these conditions, the matter dissolved from genuine Peru balsam is tolerably constant at 41 per cent., so that a sample yielding sensibly below 40 per cent., under these conditions, may be fairly regarded as adulterated, and the proportion of admixture can be approximately ascertained.[1] *Tolu balsam* and *benzoïn* can be detected with certainty in this manner, and can be distinguished by titrating the free acid in the portion of the original balsam soluble in ether or petroleum spirit.

---

[1] The difference in the petroleum extract multiplied by 2·5 equals the percentage of true Peru balsam present. Some confusion in the interpretation of this test would be caused by the presence of copaiba, but the portion of this

Various other tests have been devised for the detection of adulterants in Peru balsam, the following being the most noteworthy:—According to Fluckiger, if ten drops of genuine Peru balsam be rubbed in a mortar with 0·4 gramme of slaked lime, the product remains soft, kneadable, or somewhat friable, and readily divisible even after long exposure in the water-bath. All the usual adulterants, except fixed oil, occasion more or less hardening of the mass. With 10 per cent. of *storax*, a smeary, sticky paste is obtained, becoming of pilular consistence, and in two hours crumbly; with two drops of rectified spirit previously added, the mixture very rapidly becomes brittle and crumbly. In either case, the odour of storax is well marked. With 10 per cent. of *copaiba*, a very thin paste is produced, which becomes pilular in five minutes and brittle and crumbly in one hour, the odour of copaiba being well marked. With 8 per cent. of *colophony* or alcoholic extract of *benzoïn*, the mass becomes brittle or stony in five minutes. Grote finds that to obtain satisfactory and marked hardening, the sample should be treated with two drops of alcohol before mixing with the lime. MacEwan's experiments with the lime test were unsatisfactory.

According to Grote, if five drops of genuine Peruvian balsam be agitated with 3 c.c. of ammonia of 0·96 specific gravity, the mixture becomes brownish-grey, gives very little froth, and does not gelatinise if allowed to stand for twenty-four hours. If 20 per cent. or upwards of *colophony* be present, a very voluminous froth will be produced, and the mixture will gradually gelatinise, so that in fifteen or twenty minutes the tube may be inverted without loss of the contents. With 8 per cent. of colophony, the froth occupies twice the volume of the liquid, but no gelatinisation occurs. According to Schlickum, if an ethereal solution of Peru balsam be shaken with ammonia (specific gravity 0·96), two yellowish-brown layers are formed, between which yellowish flakes swim. On separating the ethereal layer and evaporating it, about 80 per cent. of the sample taken is obtained as a brown balsamic residue, while the ammonia retains free cinnamic acid, which is precipitated on adding excess of acid but dissolves on boiling. Benzoïn behaves somewhat similarly, but the resins of *colophony* and *copaiba* combine with the

adulterant soluble in petroleum ether is liquid and has a density and other characters approximating to those of oil of turpentine, while the petroleum ether extract from Peruvian balsam consists almost entirely of crystalline cinnamein, which is denser than water.

ammonia, and on acidifying are precipitated and not redissolved by boiling. *Castor-oil*, on the contrary, passes completely into the ether, so that no sensible precipitate is obtained by acidulating the ammoniacal liquid. A mixture of equal parts of *storax* and Peruvian balsam yields a stiff homogenous jelly when the ethereal solution is shaken with ammonia. With a smaller proportion of storax, more or less separation into layers occurs, but gelatinous lumps float in the ethereal solution, and on acidulating the separated ammoniacal solution solid resin is precipitated. (P. MacEwan did not obtain this reaction.)

If Peru balsam be rubbed in a mortar with twice its measure of concentrated sulphuric acid, a frothing and odour of sulphur dioxide will be observed if *copaiba* (15 per cent.) or certain other adulterants be present. If the cooled mixture be washed with cold water, the residue should be at first plastic, and afterwards hard and brittle. A smeary consistency points strongly to an admixture of *castor-oil*. If the washed resinous mass be treated with two or three times its weight of ether, it should dissolve completely, an insoluble residue indicating the presence of storax or benzoïn. The residue from *benzoïn* amounts to half the weight of the drug originally present, and is soluble in alcohol or (preferably) acetone; while if treatment with one of these solvents leaves a white residue of styrogenin, soluble in chloroform and separating on evaporation in microscopic crystals, *storax* is present. 7 parts of styrogenin are said to represent 100 of storax.

Various other suggestions for determining the proportions of adulterants in Peruvian balsam are detailed by Schlickum (*Pharm. Jour.*, [3], xiii. 323).

Cinnamic Aldehyde.

$$C_9H_8O. = C_8H_7.COH.$$

This compound, the only known member of the series, occurs naturally in the oils of cassia and cinnamon, of which it constitutes the greater part. It may be produced artificially by the oxidation of cinnyl alcohol; by the dry distillation of a mixture of cinnamate and formate of calcium; and by saturating a mixture of benzaldehyde and acetaldehyde with hydrochloric acid, thus:—

$$C_6H_5.COH + CH_3.COH = H_2O + C_6H_5.CH{:}CH.COH.$$

Cinnamic aldehyde is a colourless oil, rather denser than water. It may be distilled in a vacuum, or with water free from air. On exposure to the air, it quickly becomes yellow and resinous, and acquires an acid reaction. It rapidly absorbs oxygen, especially in presence of moisture, and is converted into cinnamic acid. Chromic acid converts it into benzoic and acetic acids.

Cinnamic aldehyde forms a crystalline compound with strong nitric acid, which is decomposed by the least rise of temperature, and is immediately resolved into its constituents on addition of water.

With acid sulphites of the alkali-metals, cinnamic aldehyde yields crystalline compounds similar to those formed by benzoic and other aldehydes.

Oil of Cinnamon. Oil of Cassia.

The volatile oil of cinnamon is prepared by distilling the chips and refuse bark with water. The British and French Pharmacopœias only recognise the product from Ceylon cinnamon, while the German Pharmacopœia only admits the oil from Chinese cinnamon (cassia), and in the United States the oil from both sources is recognised under the name of oil of cinnamon. Ceylon cinnamon yields from ½ to 1 per cent. of oil, and Chinese cinnamon from ½ to 1½ per cent.

The oil of Ceylon cinnamon is a pale yellow or reddish liquid, becoming red-brown and thicker on exposure to air, and finally separating crystals of cinnamic acid. It has a strong, but agreeable, cinnamon odour, and a sweet pungent, aromatic taste. The specific gravity is about 1·035, but increases with the age of the oil. It remains clear at −10° C., but at a lower temperature (−20° C.) separates a stearoptene. It is readily soluble in alcohol, but not in cold petroleum spirit, and when fresh is neutral to litmus, becoming acid by oxidation due to age or exposure.

The oil of Chinese cinnamon, commonly known as *oil of Cassia*, closely resembles the Ceylon product, except that its colour is deeper, its odour less delicate, its taste less sweet, and its specific gravity somewhat higher,—usually between 1·055 and 1·065. No sharp distinction exists between the two oils, or one which would enable one to be detected with certainty in presence of the other.

Both varieties of cinnamon oil consist chiefly, and sometimes almost entirely, of cinnamic aldehyde, but contain, in addition, small but variable proportions of hydrocarbons, and, when old, resin and cinnamic acid. To isolate the cinnamic aldehyde, the oil should be agitated with four times its volume of a saturated solution of acid potassium sulphite, which is preferable to the sodium salt. A crystalline mass rapidly forms, which is separated from the mother-liquid, washed several times by trituration with cold spirit, and then treated at a gentle heat with dilute sulphuric acid. The crystalline compound is thus decomposed, and the liberated cinnamic aldehyde can be measured, and purified by washing and drying.

Oil of cinnamon is sometimes mixed with the oil of cloves or of cinnamon leaves. These admixtures are indicated by the acrid vapours evolved on heating. According to the German Pharmacopœia, "a solution of 4 drops of oil of cinnamon in 10 c.c. of alcohol should, on the addition of 1 drop of test solution of ferric chloride, give merely a brown but not a green or blue colour (carbolic acid, oil of cloves, &c.)."

Oil of cinnamon leaves is a rather viscid, brown liquid, having a specific gravity of 1·053, and a strong clove-like and faint nutmeg-like odour. After treatment with potassa, the odour of the oil resembles that of cinnamon. A terpene, eugenol, and a little benzoic and cinnamic acid have been found in the oil.

Hager agitates oil of cinnamon with an equal measure of petroleum spirit, which dissolves the usual adulterants. Heppe confirms this, but adds that copaiba resin cannot thus be detected.

Coumaric Acid. Ortho-hydroxycinnamic Acid.

$$C_9H_8O_3 = C_6H_4(OH).CH{:}CH.COOH.$$

Coumaric acid occurs, together with melilotic or hydrocoumaric acid, $C_6H_4(OH).CH_2.CH_2.COOH$, in the yellow melilot and in the leaves of *Angræcum fragrans*. It is most easily prepared by boiling its anhydride, coumarin, with potash. Coumaric acid crystallises in brilliant prisms, which melt at 195°, and are easily soluble in water and alcohol. The solutions of its alkali-metal salts exhibit a bright green fluorescence. By fusion with potash, it yields salicylic and acetic acids, and by nascent hydrogen is reduced to melilotic acid.

COUMARIC ANHYDRIDE or COUMARIN, $C_9H_6O_2$, is the odoriferous principle of the Tonka bean, sweet woodruff, the flowers of *Anthroxanthum odoratum*, and several other plants, from which it may be extracted by alcohol. It is now manufactured artificially by heating sodium salicylic aldehyde with acetic anhydride and a little sodium acetate. On pouring the product into water an oil separates which on distillation splits up into acetic acid and coumarin. Coumarin crystallises in slender, colourless needles, melting at 67°, boiling at 290–291°, and distilling without decomposition at a higher temperature. It has a pleasant, fragrant odour and burning taste, is very slightly soluble in cold water, but more soluble in hot water and in alcohol. It also dissolves readily in ether, glycerin, oils, &c., and in strong alkalies. By prolonged boiling of the last solution coumaric acid is formed.

Coumarin exists in the Tonka bean in the proportion of 1 to 1½ per cent. It is the odoriferous principle of the scent known as "extract of new-mown hay."

PHTHALIC ACIDS.

Monocarbobenzoic Acids. Benzene-dicarboxylic Acids.

$$C_8H_6O_4 = H_2C_8H_4O_4 = C_6H_4 : \begin{cases} CO.OH \\ CO.OH. \end{cases}$$

Three isomeric acids of the above constitution are known, differing from each other in their properties and sources. Thus, on oxidation with dilute nitric acid, or an alkaline solution of potassium permanganate, the three isomeric xylenes, $C_6H_4(CH_3)_2$, yield the corresponding phthalic acids. Hence the differentiation of the latter bodies affords, in this as in many other cases, a valuable means of distinguishing between allied or isomeric bodies of the aromatic series, and of studying their constitution. The following table shows the chief points of distinction between the isomeric phthalic acids.

	Orthophthalic or Ordinary Phthalic Acid.	Metaphthalic or Isophthalic Acid.	Paraphthalic or Terephthalic Acid.
Formula.	$C_6H_4 \begin{cases} COOH^{(1)} \\ COOH^{(2)}. \end{cases}$	$C_6H_4 \begin{cases} COOH^{(1)} \\ COOH^{(3)}. \end{cases}$	$C_6H_4 \begin{cases} COOH^{(1)} \\ COOH_{(4)}. \end{cases}$
Chief sources and modes of formation.	Oxidation of ortho-xylene, alizarin, purpurin, benzene, naphthalene, and naphthalene dichloride.	Oxidation of meta-xylene and colophony.	Oxidation of para-xylene, turpentine oil, cymene, eucalyptus oil, &c.
Crystalline form.	Monoclinic prisms or nacreous laminæ.	Slender hair-like needles.	Amorphous or crystalline powder.
Melting point.	184°.	Above 300°.	Sublimes without melting.
Solubility in water.	Cold, 1 in 120 parts; boiling, more easily soluble.	Cold, 1 in 7800; boiling, 1 in 460 parts.	Cold, very slight; boiling, sparingly.
„ alcohol.	1 in 10 parts.	Readily.	Very slight.
„ ether.	3 in 2 parts.	...	Insoluble.
Action of chromic acid mixture.	Completely oxidised.	Not affected.	Not affected.
Barium salt.	Small scales or silky needles, only slightly soluble in hot water.	Crystallises in readily soluble needles.	White granular powder or concentrically arranged tablets, soluble in 350 parts of cold water.
Silver salt.	Crystalline and moderately soluble; detonates when heated rapidly.	Amorphous precipitate; forms Pharaoh's serpents on heating.	Amorphous precipitate, blackening in the light.

Orthophthalic Acid.

Ordinary phthalic acid is now manufactured on a large scale by converting naphthalene into the tetrachloride,[1] and heating this with 5 or 6 parts of nitric acid of specific gravity 1·36, till entirely dissolved, when the excess of nitric acid is expelled, and the phthalic acid crystallises out on cooling. It may be purified by re-crystallisation from hot water. The yield by this process is about 30 per cent. of the naphthalene used. Phthalic acid may also be obtained by treating naphthalene direct with nitric acid of 1·15 specific gravity, but only about 40 per cent. of the theoretical yield is obtained. Many of the properties of phthalic acid have already been described. The melting-point according to Lossen is 184°, while Ador states that the crystals melt at 213° and the powder at 203°. The discrepancies are doubtless due to the fact that phthalic acid when strongly heated loses H_2O, and forms phthalic anhydride. Neither iso- nor tere-phthalic acid forms an anhydride.

Phthalic acid is readily extracted from aqueous liquids by agitation with ether or benzene.

When heated with a single equivalent of lime, phthalic acid yields calcium benzoate and carbonate:—$2C_8H_6O_4 + 2CaO = Ca(C_7H_5O_2)_2 + CaCO_3 + H_2O$. When heated with a larger proportion of lime or other strong base, phthalic acid yields a carbonate and benzene:—$C_8H_6O_4 + 2CaO = 2CaCO_3 + C_6H_6$.

By treatment with fuming nitric acid, phthalic acid is converted into nitrophthalic acid, $C_8H_5(NO_2)O_4$, but by chromic acid mixture it is completely oxidised.

By treatment with zinc and acetic acid, phthalic acid is converted into phthalide, $C_6H_4\left\{\begin{matrix}CH_2\\CO\end{matrix}\right\}O$, diphthalyl, $C_{16}H_8O_4$, being also formed.

When treated in warm alkaline solution with sodium amalgam, phthalic acid is reduced to hydrophthalic acid, $C_8H_8O_4$,[2] which crystallises in tables, dissolves easily in hot water and alcohol, melts with decomposition at about 200°, and is converted into benzoic acid by treatment with chromic acid, nitric acid, or bromine and water.

---

[1] **Naphthalene Tetrachloride**, $C_{10}H_8Cl_4$, is manufactured by grinding naphthalene and potassium chlorate or bleaching powder with water, making the paste into balls, and bringing these after drying into concentrated hydrochloric acid. Another method consists in passing chlorine gas through melted naphthalene, taking care that the temperature does not rise above 160–170° C.

[2] Meta- and para-phthalic acids are not reduced by sodium amalgam in the cold, but on heating they both yield tetrahydro acids, $C_8H_{10}O_4$, no intermediate product being formed (*Jour. Chem. Soc.*, lii. 370).

When phthalic acid is distilled with aniline it is converted into phenyl-thalimide or phthalanil, $C_8H_4O_2(NC_6H_5)$, a body crystallising from alcohol in needles melting at 205°, but volatile at a lower temperature. It has been recommended as a febrifuge.

Phthalic Anhydride. Phthalic Oxide.

$$C_8H_4O_5 = C_6H_4 : \left\{ \begin{matrix} CO.O \\ CO.O \end{matrix} \right\} O.$$

Phthalic anhydride is prepared by heating phthalic acid to about 200° in a current of air or carbon dioxide, when the anhydride sublimes in long, white, pliant, rhombic needles. It melts at 128° and boils at 284°·5 C. It is only very slightly soluble in cold but more readily in hot water, and is reconverted into phthalic acid by prolonged boiling with water and more readily in presence of alkalies.

Phthalic anhydride derives its chief practical interest from the ease with which it reacts with phenols and their allies to form colouring matters called phthaleïns. Thus, when resorcinol, $C_6H_4(OH)_2$, is heated with excess of phthalic anhydride to about 200° C. for half an hour, the mixture acquires a yellowish-red colour, and contains the anhydride of resorcinol-phthaleïn, or fluoresceïn, $C_{20}H_{10}O_5$. The melt dissolves in dilute caustic soda or ammonia with dark red colour, the solution changing on dilution to reddish-yellow and yellow, and exhibiting after dilution a fine yellowish-green fluorescence, which is visible in solutions so weak as to appear colourless by transmitted light. On acidulating the solution and agitating with ether, the fluoresceïn is taken up, and will be again dissolved on agitating the ethereal solution with soda. If phloroglucol be substituted for resorcinol a yellow liquid is obtained, while pyrogallol yields a blue; but neither is fluorescent. The blue colour due to pyrogallol may be destroyed by cautious addition of permanganate, which acts only slowly on fluoresceïn. Catechol-phthaleïn, formed by gently heating catechol with phthalic anhydride and a little sulphuric acid, dissolves in caustic alkali solution with fine blue colour. Quinol-phthaleïn, or quinizarin, formed in a similar manner, dissolves in alkalies with violet-blue colour. If the solution be acidulated with sulphuric acid it becomes red, and the quinizarin may be extracted by agitation with ether, and recovered from the ethereal solution by shaking with caustic soda, the solution of which acquires a violet-blue colour.

The phthaleïns are described more fully in the chapter on "Dyes and Colouring Matters."

SALICYLIC ACID.

Ortho-hydroxybenzoic Acid.

$$C_7H_6O_3 = C_7H_4O(OH)_2 = C_6H_4 \begin{cases} OH^{(1)} \\ CO.OH^{(2)}. \end{cases}$$

Salicylic acid was originally prepared from salicin, $C_{13}H_{18}O_7$, a bitter principle existing in willow-bark. It may also be obtained from the oil of wintergreen, which consists essentially of methyl salicylate (page 58), by distillation with potash. It is now prepared on a considerable scale by a process due to Kolbe, based on the reaction of carbon dioxide on sodium phenate.[1] The identity of the natural acid with the purified artificial product is fully established.

When potassium phenate is acted on by carbon dioxide it reacts in a similar manner to the sodium phenate in Kolbe's process, yielding pure dipotassium salicylate up to 150°; but above that temperature the isomeric para-hydroxybenzoate is also produced, and at 220° is the sole product. Mono-potassium salicylate is converted into the basic para-hydroxybenzoate and phenol when heated to 220°, whereas the corresponding sodium salt yields the *ortho*-hydroxybenzoate or salicylate, together with phenol.

---

[1] The following is an outline of Kolbe's process :—Crude soda lye of known strength is exactly saturated by crystallised carbolic acid, and the liquid cautiously evaporated till the residue is perfectly dry. It is then subjected to the action of a stream of carbon dioxide gas at a temperature commencing at 100° C., which is gradually raised to 180°, and may reach 220° or 230° C. towards the close of the operation. During this process, carbolic acid distils over and ultimately amounts to about half the quantity taken. The residue in the retort is basic sodium salicylate, the solution of which on fractional precipitation with hydrochloric acid yields impure salicylic acid. The first portions thrown down are contaminated with resinous and colouring matters, and are rejected. The remainder of the precipitate is washed, recrystallised from hot water, and distilled at 170° C. in a current of superheated steam, when it is obtained perfectly white. If carbolic acid containing cresylic acid be used, the salicylic acid contains cresotic acid (see page 55), which possesses many of the properties of salicylic acid; but for internal medicinal use pure salicylic acid should be employed.

The reaction between sodium phenate and carbon dioxide in the cold results in their direct union with formation of sodium phenylcarbonate, $(C_6H_5)O.CO.ONa$, a white powder decomposed by water into phenol and sodium hydrogen carbonate. On heating this compound to 130° it undergoes direct molecular transformation in mono-sodium salicylate, $C_6H_4(OH).CO.ONa$. The formation of phenol and basic salicylate is due to the reaction of this salt at a high temperature with unchanged sodium phenate:—$C_6H_4(OH)CO.ONa + C_6H_5.ONa = C_6H_4(ONa).COONa + C_6H_5.OH$. The more advantageous reaction can be realised on a manufacturing scale by treating perfectly dry sodium phenate with the requisite quantity of carbon dioxide under pressure (either employing the gas or solid substance), the temperature being kept down artificially. On heating the product for several hours to 120°–130°, it is transformed into mono-sodium salicylate without separation of phenol. Operating in this manner salicylic acid can be obtained from half the quantities of soda and phenol which are required if Kolbe's process be adhered to (R. Schmitt, *Jour. Soc. Dyers*, &c., ii. 114).

Salicylic acid crystallises from alcohol in large monoclinic prisms, but usually occurs as a granular powder, consisting of minute, broken, acicular crystals, having a sweetish, acidulous, acrid taste. It has a specific gravity of 1·483, melts at 155°–156°, and when gradually heated sublimes at about 200° in slender shining needles, but when heated rapidly with powdered glass or sand it is resolved into phenol and carbon dioxide. It volatilises readily in a current of steam at 60–80 lbs. pressure, and even vaporises on boiling its aqueous solution.

Salicylic acid is a powerful antiseptic, and, owing to its slight taste, is employed for preserving beer, wine, milk, lime and lemon juices, gum, and other fluids.[1]

Salicylic acid is soluble with tolerable facility in hot water, but separates for the most part on cooling. Its solubility in cold water is variously stated at from 1 part in 300 up to 1 part in 1000. By the presence of various neutral salts, its solubility in cold water is increased without its antiseptic value being interfered with.[2] Salicylic acid is very soluble in solutions of borax, a compound of the formula $Na(BO)2C_7H_5O_3$ being said to be formed. The liquid soon undergoes decomposition.

Salicylic acid is soluble in alcohol (1 in 2½), amylic alcohol (1 in 4), ether (1 in 2), chloroform and benzene (1 in 80). It may be

---

[1] The use of salicylic acid for preserving articles of food is forbidden in France and some other countries. One part acid to 10,000 of beer or wine is the maximum proportion necessary for the preservation of the liquid.

HYDROXYNAPHTHOIC ACID, or Oxynaphthoic Acid, $C_{10}H_6(OH).COOH$, is a body which bears the same relation to naphthalene that salicylic acid bears to benzene. It is produced by the action of carbon dioxide on perfectly dry sodium alpha-naphthol at 130°. It forms colourless acicular crystals melting at 185° C. and requiring 30,000 parts of cold water for solution. Its salts give a blue coloration with ferric chloride. The corresponding acid from beta-naphthol melts at 235° and gives a violet-black colour with ferric chloride. Both varieties of hydroxynaphthoic acid are said to be powerful antiseptics, retarding the putrefaction of blood and urine much more perfectly than salicylic acid (*Pharm. Jour.*, [3], xviii. 537, 823).

[2]

Mixed with	1 part potassium nitrate,	it dissolves in	50	parts of cold water.
,,	1½ part ammonium citrate,	,,	60	,,
,,	2 parts sodium sulphite,	,,	50	,,
,,	2 parts sodium phosphate,	,,	50	,,
,,	2½ parts sodium phosphate,	,,	12½	,,

conveniently crystallised from hot petroleum spirit. Agitation with ether or chloroform removes salicylic acid from its aqueous solutions. H. Taffe recommends a mixture of ether and petroleum ether for this purpose.

Heated with water under pressure to 230° C., salicylic acid is split up into phenol and carbon dioxide:—$C_7H_6O_3 = C_6H_6 + CO_2$. On heating with concentrated hydrochloric or dilute sulphuric acid the change occurs at a lower temperature (140°–150°).

The distillation of salicylic acid with excess of lime produces calcium carbonate and phenol. In aqueous alkalies salicylic acid readily dissolves, forming salicylates. The salicylates are well-defined salts, and have met with considerable application in medicine (page 57).

ANALYTICAL REACTIONS OF SALICYLIC ACID.

Concentrated sulphuric acid dissolves pure salicylic acid without colour, forming a sulpho-acid. Impure salicylic acid gives a yellowish-brown coloration.

Cold concentrated nitric acid forms nitro-salicylic acid; with fuming nitric acid, picric acid results.

Bromine gives a reaction with salicylic acid indistinguishable from that produced by phenol, and the same is true of its behaviour with Millon's reagent (vol. ii. page 540). When boiled with excess of baryta water salicylic acid is precipitated as a basic barium salt.

Sodium amalgam gradually reduces salicylic acid in a warm, slightly acidulated solution, to its aldehyde, recognisable by its odour (page 60).

Silver nitrate and lead acetate give white precipitates with neutral salicylates, but not with free salicylic acid.

With a solution of cupric sulphate, H. Schultz states that salicylates and free salicylic acid give an emerald-green coloration, visible in 2000 parts of water and destroyed by ammonia or acid.

Fehling's solution is reduced by salicylic acid, and under favourable circumstances may be employed for its determination.

On heating salicylic acid or one of its salts with methyl alcohol and sulphuric acid, methyl salicylate is formed, having an agreeable aromatic odour (see page 58).

C. O. Curtman (*Jour. Chem. Soc.*, lii. 185) recommends the formation of methyl salicylate for the detection of salicylic acid in wine or beer. He directs that 4 c.c. of the liquid to be tested should be mixed with 2 c.c. of methyl alcohol (or failing this, ordinary alcohol), and then 2 c.c. of pure sulphuric acid cautiously added. The liquid is then agitated, heated for two minutes, allowed to cool for ten minutes, and then heated just to boiling, when if salicylic acid were present, a distinct odour of wintergreen oil will be perceptible. With traces, it may be necessary to allow the liquid to cool again, and then heat a third time. In examining condensed milk, &c., by this process, the sample should be digested for some hours with dilute alcohol, and the filtered liquid concentrated and heated as above.

Free salicylic acid may be determined alkalimetrically, using litmus or phenolphthaleïn as an indicator.

The most delicate reaction for salicylic acid is that with ferric chloride, which produces a beautiful violet colour even in extremely dilute solutions. The colour is destroyed by acids and by alkalies. The reaction is greatly more delicate (1 in 100,000) than that of phenol with the same reagent (1 in 3000).

Weiske proposes to employ the above reaction in alkalimetry. On neutralising an acid solution to which a trace of salicylic acid and ferric chloride have been added, the violet colour becomes gradually more developed until neutrality is reached, when the liquid turns reddish-yellow. But Pagliani has shown that the amount of mineral acid required for the destruction of the violet colour varies greatly with the nature of the acid and the dilution of the liquid, and hence salicylic acid is ill-suited for use as an indicator.

For the detection of salicylic acid in *milk*, H. Pellet dilutes 200 c.c. with an equal measure of water, heats to 60° C., and treats with 1 c.c. of acetic acid and an excess of mercuric nitrate free from mercurous salt. The salicylic acid is extracted from the filtered liquid by agitation with ether. A simpler plan, which suffices for rough purposes, is that of A. Remont, who agitates 20 c.c. of the milk with two or three drops of sulphuric acid, so as to break the coagulum and produce a nearly homogeneous mixture. This is shaken with 20 c.c. of ether, which after separation is evaporated, and the salicylic acid dissolved out of the residue by boiling with 10 c.c. of rectified spirit. To detect the salicylic acid in the ethereal or spirituous solution obtained, it is often sufficient to shake with a solution of ferric chloride, when the characteristic violet coloration will be produced. A more delicate and satisfactory plan is to agitate the ethereal solution with weak ammonia, separate, evaporate the ammoniacal liquid at a gentle heat, and test the residue of ammonium salicylate with ferric chloride.

For the detection of salicylic acid in *wine*, *beer*, or *urine* the liquid should be treated with excess of acetate of lead, the filtrate precipitated with dilute sulphuric acid, and the liquid again filtered and shaken with ether, preferably after concentration.[1] Lime- and lemon-juice may be treated in the same way, or may at once be agitated with ether.

---

[1] Blas recommends that the beer should be drunk and the urine tested three hours afterwards by addition of ferric chloride. The reaction is said to be five times as delicate with urine as with the original beer.

H. Taffe recommends a mixture of equal measures of ether and petroleum ether for extracting salicylic acid, as such a solvent does not take up water or tannic acid, though somewhat liable to form an emulsion.

Another method of separating salicylic acid from liquids containing it is by distillation. Wine or beer should be rendered alkaline with soda, reduced to one half by boiling, to drive off the alcohol, and then acidulated with sulphuric acid and distilled. The distillate may be rendered alkaline with soda and concentrated to a small bulk before acidulating and shaking with ether, or applying other tests for salicylic acid.

The ferric chloride reaction may be employed for the colorimetric determination of salicylic acid in a manner similar to the method of Nessler for determining ammonia in water. Instead of using an aqueous solution of salicylic acid as the standard of comparison, it is preferable in all cases to add a definite amount of salicylic acid to a liquid of the same kind as that in which the salicylic acid is to be determined. Thus milk should be compared with milk, beer with beer, and urine with urine, and the standard specimen submitted to the same treatment as the sample to be compared with it. In all cases it is desirable to extract the salicylic acid with ether before applying the iron test, as many substances weaken the colour-reaction or suppress it entirely, *e.g.*, acids, alkalies, and certain neutral salts, such as phosphates, tartrates, oxalates, &c. The ferric chloride solution should be very dilute, and must be added gradually till the coloration no longer increases. With small quantities of salicylic acid an excess of ferric chloride destroys the coloration.

COMMERCIAL SALICYLIC ACID.

The salicylic acid of commerce is far purer than was formerly the case, when more or less sodium chloride, phenol, cresotic acid, and para- and meta-hydroxybenzoic acids were frequently present. Salicylic acid is stated to have been met with in America adulterated with acid potassium sulphate, gypsum, starch, sugar, &c.

The facile formation of definite crystals is a good indication of the purity of salicylic acid, the presence of foreign matters in its solutions greatly interfering with its crystallisation. When shaken up with cold concentrated sulphuric acid, salicylic acid should yield a perfectly colourless solution.

H. Kolbe gives the following method of testing the purity of salicylic acid:—Dissolve 0·5 gramme of the sample in 5 or 6 c.c.

of strong alcohol, pour the clear solution into a watch-glass, and allow it to evaporate spontaneously. The residual salicylic acid forms a ring of beautifully aggregated efflorescent crystals round the edge of the watch-glass. This mass is pure white if the acid tested be pure and re-crystallised, but yellowish or yellow if the simply precipitated acid be used. If the colour be brownish or brown, the sample is unfit for internal use.

Chloride of sodium and other mineral impurities will remain on igniting the sample.

Carbolic acid is especially liable to be present in salicylic acid which has been sublimed. It may be detected by nearly neutralising the sample with sodium carbonate, and agitating the liquid with ether. On gently evaporating the ethereal liquid, the carbolic acid may be recognised by its smell, taste, and chemical reactions.

J. Muter gives the following test for carbolic acid in samples of salicylic acid:—Boil 10 grains in half an ounce of water, cool, decant the solution, and add to it 1 minim of a saturated solution of bicarbonate of potassium, $KHCO_3$, 1 minim of aniline, and 5 drops of solution of bleaching powder, when, if carbolic acid be present, a deep blue colour will be produced. Another test for phenol is to treat 5 c.c. of a saturated aqueous solution of the sample with a crystal of potassium chlorate and 2 c.c. of hydrochloric acid. On pouring ammonia carefully on the surface of the liquid, a reddish or brownish tint will be developed if phenol be present.

CRESOTIC ACID, $C_6H_3(CH_3)(OH).COOH$, the next homologue of salicylic acid, is prepared from cresol in a similar manner to that used for obtaining salicylic acid from phenol. It closely resembles salicylic acid. Three isomeric modifications are obtainable from coal-tar cresol, corresponding to the three isomeric cresols, and melting respectively at 151°, 163°, and 177°.

The properties of salicylic acid are much modified by the presence of cresotic acid. Thus, pure salicylic acid requires about 22 parts of boiling water for solution, while samples containing cresotic acid dissolve in 14 of boiling water, or even in a smaller proportion. If to the solution so obtained about one-fifth of alcohol be added, and the liquid allowed to cool, pure salicylic acid will form separate distinct crystals not cohering together, while samples containing cresotic acid form a network or woolly mass of small or indistinct crystals.

If to the boiling aqueous solution of impure salicylic acid excess of carbonate of calcium be added, and the liquid be filtered while hot, sparingly soluble salicylate of calcium is deposited as the solution cools. When re-crystallised and decomposed by hydrochloric acid, this substance yields pure salicylic acid, having identical properties with that obtained from wintergreen oil (see page 58). If the mother-liquid from the salicylate of calcium be further concentrated, another crop of impure crystals may be obtained. There remains in solution a very soluble calcium cresotate,[1] which, on decomposition by hydrochloric acid, gives a precipitate of cresotic acid. This, when crystallised from boiling water, forms silvery plates, which are much more soluble than salicylic acid in both hot and cold water. The proportion of cresotic acid in commercial artificial salicylic acid was formerly probably sometimes as high as 25 per cent., but when pure phenol has been used for the manufacture the proportion of cresotic acid must be insignificant.

The violet reaction with ferric chloride is common to salicylic and the three cresotic acids.

Isomers of Salicylic Acid.—Salicylic acid has the constitution of an ortho-hydroxybenzoic acid. Its two isomers, the meta- and para-hydroxybenzoic acids, are said to be sometimes present in commercial samples of salicylic acid. The following table shows the chief differences of analytical value :—

	Ortho-hydroxybenzoic Acid (Salicylic Acid).	Meta-hydroxybenzoic Acid.	Para-hydroxybenzoic Acid.
Formula.	$C_6H_4\left\{\begin{matrix}OH^{(1)}\\COOH^{(2)}.\end{matrix}\right.$	$C_6H_4\left\{\begin{matrix}OH^{(1)}\\COOH^{(3)}.\end{matrix}\right.$	$C_6H_4\left\{\begin{matrix}OH^{(1)}\\COOH^{(4)}.\end{matrix}\right.$
Fusing point.	156° C.	200° C.	210° C.
Volatility.	Volatilises with steam when the aqueous solution is distilled.	Not volatile with the vapour of water.	Not volatile with the vapour of water.
Solubility in water at 0° C.	1 in 1100.[2]	1 in 265.	1 in 580.
Solubility in water at 15° C.	1 in 1000.	1 in 120.	1 in 126.
Reaction with ferric chloride.	Deep violet colour.	No change.	Yellow precipitate, soluble in excess.
Heated in a current of dry ammonia gas.	Yields phenol, CO_2, &c.	Yields oxybenzonitril, $C_6H_4(OH).CN$, melting at 82° C.	Yields phenol, CO_2, &c.
Antiseptic properties.	Strong.	None.	None. (?)

Salicylic acid prevents the precipitation of copper salts by alkalies, while its isomerides have not this property.

---

[1] Excess of milk of lime cannot be substituted for the carbonate of calcium, or a sparingly soluble basic calcium cresotate results, which cannot be separated from the salicylate.

[2] According to Bourgoin (*Jour. Pharm. Chimie*, [4], xxx. 488), the solubility of salicylic acid at 0° C. is 1 part in 666, instead of the number given in the text, which is due to Ost (*Jour. Prac. Chem.*, [2], xvii. 228).

Salicylic acid may be partially separated from para-hydroxybenzoic acid, which is the isomer most likely to be present in the commercial substance, by mixing the hot aqueous solution with excess of milk of lime, when a basic calcium salicylate separates on cooling. A more exact separation may be effected by drying the free acids at 100° C., and agitating with anhydrous chloroform. Salicylic acid dissolves readily, but para- and meta-hydroxybenzoic acids remain chiefly undissolved.

From benzoic acid, para-hydroxybenzoic acid may be separated by treatment with carbon disulphide, in which the latter acid is nearly insoluble.

Metallic Salicylates.

Salicylic acid has characters intermediate between those of a phenol and an ordinary acid. The hydrogen of the carboxyl group is replaceable by metals, with formation of the salts of the formula $C_6H_4(OH).COOM$. The hydrogen of the hydroxyl group (phenolic hydrogen) is also replaceable by alkali-metals, the basic compounds so produced being converted by carbonic acid into the monobasic salicylates. Salicylic acid is monobasic with all indicators of neutrality.

The ordinary or neutral metallic salicylates are well-defined salts, and mostly crystallisable. When heated in the solid state they evolve phenol and carbon dioxide. The residue usually consists of a basic salicylate, but in the case of the potassium compound much para-hydroxybenzoate (page 56) remains. Secondary products are also liable to be formed.[1]

Solutions of the neutral salicylates give an intense violet coloration with ferric chloride, and respond to the other reactions for salicylic acid (page 52).

On adding dilute sulphuric or hydrochloric acid to a solution of a salicylate, salicylic acid is thrown down as a bulky white precipitate, readily dissolved on agitation with ether.

SODIUM SALICYLATE, $2NaC_7H_5O_3+H_2O$, forms small white crystalline plates or a crystalline powder permanent in the air, odourless, having a sweetish saline and somewhat alkaline taste, and neutral or feebly acid reaction to litmus. It is soluble in 1½ parts of cold water, only slightly soluble in absolute alcohol, but soluble in 8 parts of cold rectified spirit. In boiling water and alcohol it is very soluble. Both the alcoholic and the aqueous solution give a violet colour with ferric chloride. On ignition, sodium salicylate evolves phenol, and leaves from 30 to 31 per cent. of Na_2CO_3. It is completely soluble in ammonia, and the solution does not reduce nitrate of silver, even on boiling. Barium chloride should cause no precipitate in the aqueous solution, and the precipitate with nitrate of silver should completely dissolve on addition of nitric acid and alcohol. When the solid salt is shaken in the cold with 15 parts of strong sulphuric acid, no brown coloration should be produced. Sodium salicylate is liable to become coloured by keeping, especially if exposed to the air. The change of the solution may be prevented by the addition of a small proportion (1 per cent.) of sodium thiosulphate.

---

[1] Phenolsulphonates also evolve phenol when heated, but the residue contains sulphate, at any rate if nitrate or carbonate of sodium be added before igniting.

FERRIC SALICYLATE, $Fe(C_7H_5O_3)_3$, separates, on mixing a strong solution of sodium-salicylate with ferric chloride, as a brown precipitate, which, together with the mother-liquor, rapidly acquires a deep violet colour. After washing, ferric salicylate forms a brown amorphous body, which yields a violet solution on boiling with water.

BISMUTH SALICYLATE, which is used in medicine, is of very inconstant composition, the proportion of Bi_2O_3 ranging from 35 to 73 per cent. (*Pharm. Jour.*, [3], xv. 889).

Salicylic Ethers.

Several of the ethereal salts of salicylic acid have a practical interest.

METHYL SALICYLATE, $C_8H_8O_3 = C_6H_4(OH).CO.O(CH_3)$. This ether constitutes the greater part of the natural essential oils of *Gaultheria procumbens, Betula lenta,* cherry-birch, and some other plants, and may be obtained therefrom by distilling the plants with water.

Methyl salicylate may also be prepared artificially by distilling salicylic acid or a salicylate with methyl alcohol and strong sulphuric acid.

Methyl salicylate is a colourless, oily liquid (becoming red on keeping), of strong and agreeable odour, and sweet, cooling, aromatic taste. It has a density of about 1·18 and boils at about 220° C., the hydrocarbon with which it is associated in gaultheria oil boiling about 20° lower. Methyl salicylate is slightly soluble in water, and is miscible in all proportions with alcohol and ether.

On adding a concentrated solution of caustic potash or soda to the oil, combination immediately ensues, with liberation of heat, and white crystalline compound is formed, $C_6H_4(OK)COO(CH_3)$, which is decomposed by acids with separation of the original oil. When boiled with strong potash solution methyl salicylate is saponified, with formation of potassium salicylate and methyl alcohol.

The aqueous and alcoholic solutions of methyl salicylate give the characteristic violet coloration with ferric chloride.

Commercial Gaultheria Oil is a name applied indifferently to the products from the wintergreen and cherry-birch, though the two products are not absolutely identical. The true gaultheria oil contains more or less (from an insignificant quantity up to 10 per cent.) of a hydrocarbon isomeric with turpentine oil (boiling about 200° C.), which somewhat modifies its odour, density, and boiling point. The oil of cherry-birch, on the contrary, consists of practically pure methyl salicylate.

Gaultheria oil is now sometimes employed in medicine as a substitute for the metallic salicylates. It is liable to adulteration with oil of sassafras, alcohol, and chloroform.

Chloroform may be detected by the smell when the sample is warmed. Samples containing chloroform have a high density and low boiling point, while the density is diminished by the presence of *alcohol*. The chloroform may be approximately separated and determined by fractional distillation, or by estimating the hydrochloric acid formed on passing the vapour mixed with hydrogen through a red-hot tube. In the portion from which the alcohol and chloroform have been separated by distillation, oil of sassafras may be recognised by its odour after addition of a hot concentrated solution of caustic potash, which combines with the gaultheria oil. *Sassafras oil* may also be detected by adding 3 or 4 drops of nitric acid (of 1·3 to 1·4 sp. gr.) to 4 or 5 drops of the oil. Sassafras oil becomes blood-red in colour, and soon changes to a brown or dark red amorphous mass. Pure oil of wintergreen is unchanged at first, but after some hours it solidifies to a mass of colourless crystals, consisting of methyl-nitrosalicylic acid.

Artificial methyl salicylate is now prepared of high purity, and appears likely to replace the natural substance. According to C. Bullock, on shaking a few drops of the artificial oil with water, a "tinted" mixture is formed which does not separate for some time, while the natural oil separates almost immediately in clear drops. The behaviour of the artificial product with water is said to be due to the presence of methylic ether, $(CH_3)_2O$, and when this is washed out the separation from water occurs more quickly.

PHENYL SALICYLATE. SALOL. $C_6H_4(OH).CO.O.C_6H_5$. This body is now manufactured by heating the product of the action of carbon dioxide on sodium phenate with phosphorus oxychloride or pentachloride, when phenyl salicylate and metaphosphate and chloride of sodium result. Phosgene gas (carbon oxychloride) may be substituted for phosphorus pentachloride (*Jour. Soc. Chem. Ind.*, v. 677).

Phenyl salicylate crystallises in rhombic prisms which melt at 42°–43° C. It usually occurs as a white crystalline powder of very faint aromatic odour, but the dilute alcoholic solution has a smell resembling that of wintergreen oil, probably owing to the formation of traces of ethyl salicylate. It is almost tasteless, and nearly insoluble in water, but dissolves in alcohol, ether, chloroform, petroleum spirit, and liquefied carbolic acid.

The alcoholic solution of salol is coloured violet by ferric chloride, while bromine gives a precipitate in the form of long needles, consisting of a bromo-derivative, $C_{13}H_9O_3Br$, crystallising from alcohol in silky needles which melt at 98°·5 C. When boiled with caustic soda, salol is readily saponified, and the solution when acidulated with hydrochloric acid gives an odour of phenol and a copious precipitate of salicylic acid, which after filtration and washing with cold water gives with hot water a solution rendered violet by ferric chloride.

Salol should not redden moistened litmus-paper; and when shaken with 50 parts of water should give a filtrate which is not rendered violet on addition of one drop of ferric chloride, nor any immediate change on adding silver nitrate or barium chloride.

Salol is employed in medicine as a substitute for metallic salicylates and wintergreen oil. Being insoluble it passes unchanged through the stomach, but in the duodenum is decomposed into phenol and salicylic acid, and these products can be detected in the urine, which is usually very dark in colour. As an antipyretic, antiseptic, and antirheumatic, salol possesses properties of value. When applied externally it has no corrosive action, and its lower melting point gives it some advantages over salicylic acid.

A body analogous to salol may be obtained by substituting resorcinol for phenol.

NAPHTHYL SALICYLATE, $C_6H_4(OH)CO.O.C_{10}H_7^{(\beta)}$, a body analogous to salol, has been introduced into commerce under the name of "betol." It forms small, lustrous crystals, melting at 203°, almost devoid of taste, and insoluble in water but soluble in alcohol and fatty oils.

Salicylic Aldehyde. Salicylol.

$$C_7H_6O_2 = C_6H_4(OH).CO.H.$$

Salicylol was originally obtained by distilling the flowers of the meadow-sweet, *Spiræa ulmaria*, with water. It is formed by oxidation of the corresponding alcohol, saligenol, $C_6H_4(OH).CH_2OH$, and by the action of oxidising agents on such glucosides (*e.g.*, populin and salicin) as yield this alcohol by hydrolysis. It is also obtained by the action of chloroform on a strong solution of phenol in excess of caustic soda :—$C_6H_6O + 3NaHO + CHCl_3 = C_7H_6O_2 + 3NaCl + 2H_2O$.

Salicylic aldehyde is a colourless oily liquid, of pleasant aromatic odour, and having a specific gravity of 1·173 at 15°. It boils at about 196° C., and distils readily in a current of steam. It is moderately soluble in water and very readily in alcohol and ether, and is extracted from its aqueous solutions by agitation with the latter solvent. Salicylol, like other aldehydes (vol. i. p. 164), combines with the acid sulphites of the alkali-metals to form crystalline compounds, which are decomposed by dilute sulphuric acid with re-formation of salicylol. The tendency to form the acid sulphite compound is so strong that salicylol is readily extracted from its ethereal solution by agitation with a strong aqueous solution of sodium hydrogen sulphite. This reaction is of service for the separation of salicylol from salicylic acid, phenol, &c.

By oxidation, salicylic aldehyde is converted into salicylic acid, which it resembles in the deep violet coloration its solutions acquire on addition of ferric chloride.

Salicylol has sometimes been termed salicylous acid, from its power of dissolving in solutions of alkalies to form crystalline metallic derivatives. It even decomposes carbonates.

SALICYLURIC ACID, $C_9H_9NO_4 = C_6H_4(OH).CO.NH.CH_2.COOH$. This acid occurs in the urine after administration of salicylic acid, but some of the latter is excreted unchanged. It closely resembles salicylic acid, but may be separated therefrom by a mixture of ether and benzene, in which it is little soluble.

PROTOCATECHUIC ACID.

Ortho-dihydroxybenzoic Acid. Ortho-hydroxysalicylic Acid.

$$C_7H_6O_4 = C_7H_3O(OH)_3 = C_6H_3\left\{\begin{array}{l} OH^{(1)} \\ OH^{(2)} \\ CO.OH^{(4)}. \end{array}\right.$$

Protocatechuic acid results from the fusion of various organic bodies with caustic potash. Catechin and maclurin also yield phloroglucol (see page 84), while many resins give para-hydroxybenzoic acid in addition, and gum benzoïn gives protocatechuic and benzoic acids.

Protocatechuic acid forms thin monoclinic prisms or tufts of needles containing one molecule of water, which is lost at 100°. It melts at 194° and at a higher temperature is resolved into carbon dioxide and catechol, $C_6H_4(OH)_2$. Protocatechuic acid dissolves in 53 parts of cold water, and in 3½ parts at 80°. It is very soluble in alcohol, less so in ether, and almost insoluble in benzene, even when boiling. It is extracted from its aqueous solution by agitation with ether or petroleum ether.

An aqueous solution of protocatechuic acid is coloured an intense bluish-green by ferric chloride (avoiding excess), the colour being changed to blue and afterwards to dark red on adding a very dilute solution of carbonate of sodium. A neutral solution of a protocatechuate gives a violet coloration with ferrous sulphate.

Protocatechuic acid gives a white precipitate with lead acetate, and reduces ammonio-nitrate of silver when heated, but has no effect on Fehling's solution.

Besides the important class of tannins giving green colorations with ferric salts (page 78), the following homologues and derivatives of protocatechuic acid possess a practical interest:—

Orsellinic Acid (Dihydroxytoluic acid), . $CH_3.C_6H_2\left\{\begin{array}{l}OH\\OH\\CO.OH.\end{array}\right.$

Orsellic, Diorsellinic, or Lecanoric acid, . . . $CO\left\{\begin{array}{l}C_6H_2(CH_3).(OH)_2\\O.C_6H_2(CH_3)(OH).CO.OH.\end{array}\right.$

Vanillic Acid (Methylprotocatechuic acid), . . $C_6H_3\left\{\begin{array}{l}CO.OH^{(1)}\\O.CH_3^{(3}\\OH^{(4)}.\end{array}\right.$

Vanillin (Methylprotocatechuic aldehyde), . . $C_6H_3\left\{\begin{array}{l}CO.H^{(1)}\\O.CH_3^{(3)}\\OH^{(4)}.\end{array}\right.$

Piperonal (Methylene-protocatechuic aldehyde), $C_6H_3\left\{\begin{array}{l}CO.H\\\left.\begin{array}{l}O\\O\end{array}\right\}:CH_2.\end{array}\right.$

Catechol (Pyrocatechin), ... $C_6H_4\left\{\begin{array}{l}OH^{(1)}\\OH^{(2)}.\end{array}\right.$

Guaiacol (Methyl catecholate), ... $C_6H_4\left\{\begin{array}{l}O.CH_3\\OH.\end{array}\right.$

Vanillin. Vanillic Aldehyde. Methylprotocatechuic Aldehyde.

$$C_8H_8O_3=C_6H_3\left\{\begin{array}{l}COH^{(1)}\\O(CH_3)^{(3)}\\OH^{(4)}.\end{array}\right.$$

Vanillin is the odoriferous principle of vanilla (the fruit of *Vanilla aromatica*). It is produced artificially from coniferin, $C_{16}H_{22}O_8$, a glucoside occurring in the cambial secretion of all coniferous plants, by oxidation with chromic acid mixture (*Pharm. Jour.*, [3], iv. 996); or the coniferin may be split up by boiling with dilute acids or the action of emulsin into glucose, $C_6H_{12}O_6$, and coniferyl alcohol, $C_{10}H_{12}O_3$, and the latter product, oxidised by chromic acid mixture (see also, *Jour. Soc. Chem. Ind.*, iii. 530). Vanillin is also produced by the action of chloroform on an alkaline solution of guaiacol, $C_6H_4(OCH_3)OH$, a constituent of wood-tar creosote (page 66). Vanillin may likewise be prepared from eugenol, $C_{10}H_{12}O_2$, a phenoloid body which is obtained by treating oil of cloves with caustic alkali, filtering, and precipitating the solution with carbonic acid. The eugenol is treated with acetic anhydride, and the acetyl derivative oxidised by a very dilute solution of potassium permanganate. When the oxidation is sufficiently advanced, the liquid is filtered, the filtrate made slightly alkaline, concentrated at a low temperature, acidulated with sulphuric acid, and the vanillin extracted by agitation with ether.

Vanillin crystallises in stellate groups of colourless needles, melts at 80°–81°, and sublimes when cautiously heated. It has a pleasant aromatic taste and odour resembling vanilla. Vanillin dissolves sparingly in cold water, more freely in hot, and readily in alcohol and ether. Vanillin has the constitution and characters of an aromatic aldehyde. It forms well-defined bisulphite compounds, and also yields crystalline compounds with bases. Heated with dilute hydrochloric acid (preferably under pressure to 200°) it is resolved into methyl chloride, CH_3Cl, and protocatechuic aldehyde; and when fused with caustic potash is converted into protocatechuic acid.

By exposing moist and finely pulverised vanillin to the air it is oxidised to vanillic or methylprotocatechuic acid, $C_8H_8O_4$, which crystallises from ether in white laminæ, and gives no colour-reaction with ferric chloride.

Vanillin may be extracted from aqueous liquids containing it by acidulating and agitating with ether. It may then be separated from many substances simultaneously extracted by agitating the ethereal solution with a saturated solution of sodium bisulphite (see page 21).

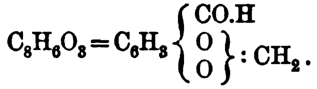
On rubbing together vanillin, resorcinol, and hydrochloric acid, a deep bluish-violet coloration is observed, which vanishes after a time.

Besides its agreeable odour, vanillin is characterised by the bluish-violet coloration produced in its solution on addition of ferric chloride. On heating the liquid, dehydro-divanillin, $C_{12}H_4(OH)_2(COH)_2(OCH_3)_2$, separates in fine white needles, melting at 304°, and sparingly soluble in water, alcohol, ether, chloroform, and benzene, but readily soluble in alkalies (Tiemann, *Jour. Soc. Chem. Ind.*, v. 252).

Vanilla is the fruit or pod of *Vanilla planifolia*, var. *aromatica*, a plant growing in Mexico, Java, Mauritius, &c. Its cultivation has become restricted since the artificial production of vanillin. Vanillin has been found in vanilla pods in proportions ranging from 1·32 to 1·86 per cent., in the Mexican product; from 0·75 to 2·90 in that from Mauritius; and from 1·56 to 2·75 in Java vanilla. These vanillas also contain vanillic acid, which was apparently mistaken for benzoic acid by the earlier investigators. Their aroma is entirely due to vanillin.[1]

For the *assay of vanilla*, from 30 to 50 grammes of the finely chopped pods should be exhausted with ether, and the ethereal solution concentrated and thoroughly agitated with its own measure of equal parts of water and a saturated solution of acid sodium sulphite. The ether is separated, and the aqueous liquid, containing the whole of the vanillin, treated with dilute sulphuric acid. The liberated sulphurous acid is expelled by a current of steam, and the residual liquid cooled and again shaken with ether. The ethereal solution is separated, distilled to a small bulk, and the remaining ether allowed to evaporate spontaneously. The residual vanillin is dried over sulphuric acid, and weighed. The process gives results from 1 to 4 per cent. below the truth (Tiemann and Haarmann, *Pharm. Jour.*, [3], vi. 603). Vanillin has been detected in assafœtida by the same process.

Piperonal. Methylene-protocatechuic Aldehyde.



$$C_8H_6O_3 = C_6H_3\left\{\begin{matrix} CO.H \\ \left.\begin{matrix} O \\ O \end{matrix}\right\} : CH_2 . \end{matrix}\right.$$

Piperonal is produced by the gradual addition of a solution of potassium permanganate to one of potassium piperate. The liquid acquires a plesant odour like that of coumarin, and yields piperonal on distillation.

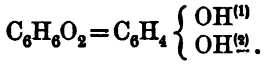
Piperonal crystallises in large lustrous prisms. It has a pungent taste and very agreeable odour, melts at 37°, and boils without change at 263°. It is sparingly soluble in cold water, but more readily in hot, in which it melts, and dissolves very easily in alcohol and ether. It behaves like an aldehyde, and forms a compound with acid sulphite of sodium which crystallises in laminæ and is but slightly soluble in water or alcohol. It is not altered by aqueous alkalies.

---

[1] On the other hand, in the West Indian variety, called *vanillone*, the vanilla (from 0·4 to 0·7 per cent.) is associated with another substance, probably of aldehydic character (benzoic aldehyde or piperonal). Vanillone has long been used for preparing "essence of heliotrope," but this is now made by adding a small quantity of benzoic aldehyde (artificial) to artificial vanillin, when, after a short time, the mixture acquires exactly the odour of the natural white heliotrope.

Piperonal has been recently recommended as an antipyretic and antiseptic of moderate power.

Catechol, Pyrocatechin. Ortho-dihydroxybenzene.



$$C_6H_6O_2 = C_6H_4 \begin{cases} OH^{(1)} \\ OH^{(2)}. \end{cases}$$

Catechol is produced by heating protocatechuic acid, and tannins and allied bodies derived from it. It is also produced by the action of an excess of fusing potash on ortho-phenolsulphonic acid, $C_6H_4(SO_3H)OH$.[1] It is best prepared by the action of hydriodic acid gas on boiling guaiacol.

Catechol forms short square prisms or thin pearly plates resembling benzoic acid. It melts at 104° and boils at 245°. It sublimes readily and condenses in brilliant laminæ. The taste is bitter, and the fumes are pungent and excite coughing.

Pyrocatechin is very soluble in water, alcohol, and ether. It is extracted from its aqueous solution by agitation with ether.

Catechol forms unstable compounds with bases. With lime-water, an aqueous solution of catechol forms a mixture which acquires a reddish or brown colour, but remains clear for some time. Caustic soda behaves somewhat similarly, the solution becoming, in succession, green, brown, and black. Catechol is not precipitated by gelatin or alkaloids. With acetate of lead it yields a white precipitate easily soluble in acetic acid. It reduces silver nitrate in the cold, and Fehling's solution on warming.

An aqueous solution of pyrocatechin gives no reaction with ferrous salts. With ferric chloride, avoiding excess, it gives a grass-green colour, which, on adding acid carbonate of sodium, is changed to a fine violet-red, not much altered by boiling but restored to green by cautious addition of acids. (These reactions distinguish catechol from pyrogallol.)

Fir-wood moistened with hydrochloric acid mixed with a solution of pyrocatechin acquires a violet-red coloration. Phloroglucol gives a similar reaction to pyrocatechin.

Guaiacol or Methyl Catecholate, $C_6H_4(OH)O.CH_3$, boils at 200°, has a specific gravity of 1·117 at 13°, is slightly soluble in water, and readily in alcohol and ether. Its analytical reactions are practically those of purified wood-tar creosote, of which, with its homologues, it forms the greater part (vol. ii. page 565). Guaiacol has recently been recommended for the treatment of phthisis (*Pharm. Jour.*, [3], xviii. 537).

---

[1] Catechol is best obtained from the fraction of beechwood-tar creosote boiling at about 200°-205°. This consists essentially of guaiacol (vol. ii. page 565), the methyl ether of catechol, $C_6H_4(OCH_3)OH$, and on heating it to the boiling point, and passing in hydriodic acid gas as long as methyl iodide distils over, catechol is produced and may be purified by fractional distillation.

GALLIC ACID.

Trihydroxybenzoic Acid. Dihydroxysalicylic Acid.

$$C_7H_6O_5 = C_6H_2(OH)_3.COOH.$$

Gallic acid occurs in gall-nuts, sumach, divi-divi, tea, hellebore-root, pomegranate, and many other plant-products. It may be obtained synthetically by fusing bromoprotocatechuic acid with potash, and by several other reactions.

Gallic acid is commonly prepared by the action of boiling dilute acid on gallotannic acid ($C_{14}H_{10}O_9 + H_2O = 2C_7H_6O_5$) or by the hydrolysis of the same body in presence of air, under the influence of a natural nitrogenised ferment called pectase. For this purpose powdered gall-nuts are moistened with water and exposed to the air for some weeks. The dark-coloured mass is washed with a little cold water and then boiled with more water, which extracts the gallic acid.

Gallic acid forms white or light brown crystalline needles, containing 1 aq., which it loses at 100° C., or, according to Böttinger, at 120°. It is soluble in 130 parts of cold, or 3 of boiling water, the hot saturated solution depositing abundant crystals on cooling. The solution has an acid and astringent taste, and decomposes on keeping. Gallic acid is also soluble in rectified spirit and in glycerin, and is slightly soluble in ether (1 in 40). It may be removed from its aqueous solution by agitation with ether or ethyl acetate.

When heated to a temperature of 210 to 220° C., gallic acid melts and is decomposed with production of carbon dioxide and formation of a crystalline sublimate of pyrogallol, $C_6H_6O_3$ (see page 70). If the heat be raised suddenly to 250° C. the results are different; in addition to carbon dioxide, water is given off, and in the retort there is found a considerable proportion of dark lustrous material, which consists chiefly of metagallic acid, ($C_6H_6O_3 = C_6H_4O_2 + H_2O$). By heating gallic acid in glycerin to about 200° C., the theoretical yield of pyrogallol is obtainable.

When heated to about 140° C., with four times its weight of concentrated sulphuric acid, gallic acid is converted into rufigallic acid.[1] Löwe uses five parts of sulphuric acid, and recommends a water-bath as the source of heat. The solution first becomes red and then purple, and on pouring the liquid into water nearly pure rufigallic acid is precipitated. If in the above process a portion of the gallic acid be replaced by benzoic acid, the product is a trihydroxyanthraquinone called anthragallol.

Gallic acid is a monobasic acid, and forms a series of crystallisable metallic salts. The gallates of the alkali-metals are permanent in a dry state and in acid solution, but in presence of free alkali they rapidly absorb oxygen, and become brown with formation of humoïd products.

Gallic acid is employed in medicine, as a reducing agent in photography, in the production of certain colouring matters, as a hair-dye, &c. It is not a tanning agent.

ANALYTICAL REACTIONS OF GALLIC ACID.

An aqueous solution of gallic acid gives the following reactions:—

On addition of ferric chloride a deep blue precipitate is formed, which is soluble in excess of the reagent with green colour. The exact colour of the precipitate is much affected by the concentration of the solutions. An exeess of gallic acid destroys the colour and reduces the iron to the ferrous state. Boiling produces a similar change.

In the absence of air a solution of ferrous sulphate gives a white precipitate with gallic acid in concentrated solution, but in dilute solution no reaction occurs. On exposure to air the liquid becomes bright blue, and deposits a black precipitate without becoming decolorised.

W. H. Ince (*Pharm. Jour.*, [3], xvii. 462) prepares a neutral ferrous chloride by decomposing cupric chloride by iron filings or wire. He adds this reagent to the solution to be tested for gallic acid, and then gradually adds bromine in excess. Operating in this manner, gallic acid gives a faint blue colour on first adding the ferrous chloride, and this is changed to indigo-blue on cautious addition of bromine water or vapour, but the liquid is decolorised on adding excess.

---

[1] RUFIGALLIC ACID or Rufigallol, $C_{14}H_8O_8$, has the constitution of a hexahydroxy-anthraquinone. It forms small, shining, reddish-brown crystals containing 2 aq., but becomes anhydrous at 220°, and sublimes at a higher temperature in cinnabar-red prisms. Rufigallic acid dissolves sparingly in hot water, alcohol, and ether. Its solution gives a brown colour with caustic alkalies, and an indigo-blue precipitate with baryta water. When heated with zinc-dust it is reduced to anthracene, $C_{14}H_{10}$.

When pyrogallol is fused with ammonium oxalate it yields ammonium rufigallate, which dissolves in water with red colour, and gives the following reactions:—Potassium ferricyanide and potassium bichromate give a dark brown precipitate insoluble in alcohol. Ferric chloride gives no black coloration, and neither sodium nitroprusside nor platic chloride produce either precipitate or change of colour. On adding a few drops of acetic acid, and then potassium cyanide and mercurous nitrate, a black precipitate is obtained. Caustic alkalies cause a change to brown but not to black.

On addition of excess of caustic alkali to a solution of gallic acid the liquid turns yellow and ultimately brown and black on exposure to the air, from formation of tanno-melanic acid. The reaction is accelerated by boiling. On neutralising the black liquid with acetic acid and adding lead acetate, a black precipitate is thrown down. If sodium bicarbonate be used instead of caustic alkali, the liquid becomes indigo-blue and deposits a deep bluish-green precipitate, turned red by acids.

Lime-water in excess produces a white precipitate, changing very rapidly to blue.

Solution of tartar-emetic, $K(SbO)\bar{T}$, precipitates white gallate of antimony, even from very dilute solutions. The reaction is prevented by chloride of ammonium.

Gallic acid does not reduce Fehling's solution, or only very slowly and imperfectly, but it reduces gold and silver solutions (rapidly when hot), and decolorises an acid solution of potassium permanganate, being oxidised to hydro-rufigallic acid, $C_{14}H_8O_5$. In the absence of other reducing agents, gallic acid may be determined by titration in an acid solution with permanganate, preferably in presence of indigo. If tannic acid be present it must first be separated by precipitation with gelatin.

No precipitate (distinction from tannic acids) is produced with gallic acid by solutions of alkaloids, gelatin, albumin, or starch, but a mixture of gum-arabic and gelatin is precipitated.

Solution of potassium cyanide produces, with gallic acid, a fine red coloration, which shortly disappears, but can be restored by agitating the liquid.

An ammoniacal solution of potassium ferricyanide produces a very bright red coloration, destroyed only on adding a large excess of the reagent.

An aqueous solution of picric acid, to which an excess of ammonia has been previously added, produces with gallic acid a red coloration, changing in a few seconds to a beautiful green.

Gallic acid gives a somewhat similar and delicate reaction on addition of a faintly alkaline solution of arseniate of sodium, when the surface of the liquid exposed to the air rapidly becomes deep green.

The following table exhibits the reactions of gallic acid in juxtaposition with those of gallotannic and pyrogallic acids, to which bodies gallic acid presents many points of resemblance :—

Reagent.	One per cent. solution of		
	Gallotannic Acid.	Gallic Acid.	Pyrogallol.
1. Gelatin, . . .	White or buff coloured precipitate.	No change, except in presence of gum-arabic.	No change.
2. Fehling's solution, on heating, . .	Yellow or red precipitate of Cu_2O.	No change, or slow and imperfect reduction.	Yellow or red precipitate of Cu_2O.
3. Ferrous sulphate (free from ferric salt), . . .	No change; white in concentrated solution, darkening on exposure.	No change; white in concentrated solution, darkening on exposure.	White precipitate changed to blue solution by least trace of ferric salt.
4. Ferric chloride, .	Blue-black precipitate; colour destroyed by boiling.	Deep blue coloration, destroyed by boiling.	Red colour, turning brown on heating.
5. Ferric acetate, .	Blue-black precipitate.	Purple-black precipitate.	Purple-black coloration.
6. Ammoniacal ferricyanide, . .	Deep red coloration destroyed by moderate excess of the reagent.	Vermillion - red coloration, only destroyed by large excess of reagent.	Intense brown coloration.
7. Ammoniacal picric acid, . . .	Reddish.	Red coloration, rapidly changing to fine green.	Reddish.
8. Lime water in excess; or barium chloride and ammonia, . . .	White precipitate, rapidly becoming blue.	White precipitate, very rapidly becoming blue.	No precipitate; immediate purple colour becoming brown in the air.
9. Lead acetate, .	White precipitate insoluble in acetic acid.	White precipitate, soluble in acetic acid.	Slight precipitate.
10. Lead nitrate, .	White precipitate.	No change.	No change.
11. Tartar emetic, .	White precipitate, insoluble in ammonium chloride.	White precipitate, soluble in ammonium chloride.	No change.
12. Bismuth nitrate, .	White precipitate.	Pale yellow precipitate.	Dark greenish precipitate.
13. Ammoniacal cupric sulphate, . .	Precipitate.	No precipitate.	Deep purple-brown coloration.
14. Potassium cyanide,	No reaction.	Red colour disappearing on standing, but restored by shaking with air.	No reaction.

In the absence of tannin and other interfering matters, gallic acid may be determined by digesting the solution with a known weight of recently ignited oxide of zinc. This is filtered off, washed, dried at 110° C., and reweighed, when the increase of weight indicates the gallic acid taken up.

Gallic acid may be separated from many varieties of tannin by agitating the aqueous solution with ether. When the tannin is soluble in ether, it may be precipitated by a moderate excess of gelatin, as in Lowenthal's process (page 109), and the gallic acid extracted from the filtrate by agitating with ether or acetic ether.

An approximate estimation of the gallic acid may be made by titrating the filtrate with standard permanganate in presence of sulphuric acid and indigo.

Another method of separating gallic acid from tannins depends on the insolubility of cupric gallate in water, and its solubility in ammoniacal liquids. The solution is precipitated by excess of cupric acetate, the precipitate washed and digested with a cold solution of ammonium carbonate. The solution, filtered from any insoluble tannate of copper, is evaporated to dryness, the residue moistened with nitric acid, ignited, and the resultant cupric oxide weighed. Its weight, multiplied by 0·9, gives the weight of gallic acid.[1] This method is applicable to the separation of gallic acid from gallotannic and quercitannic acids, but the copper salts of many varieties of tannin are more or less soluble in ammonium carbonate.

The solubility of lead gallate in acetic acid affords another means of separating gallic and tannic acids.

Pyrogallol. Pyrogallic Acid. Trihydroxybenzene.

$$C_6H_6O_3 = C_6H_3(OH)_3 = C_6H_3\begin{cases} OH^{(1)} \\ OH^{(2)} \\ OH^{(3)}. \end{cases}$$

This substance is prepared by heating gallic acid or an aqueous extract of gall-nuts to a temperature of about 210° C., when pyrogallol sublimes in prismatic plates. It may also be prepared by heating commercial gallotannic acid in glycerin to 200° C., diluting with water, and extracting the pyrogallol by agitation with ether.

When rapidly heated to 250° C. pyrogallol loses the elements of water and is converted into a black amorphous mass called metagallic acid, insoluble in water, but soluble in alkalies.

Pyrogallic acid crystallises in thin plates or white lustrous needles. It has a specific gravity of 1·463, melts at 131° C.,[2] and sublimes at a higher temperature. It has an acid and very bitter taste. Pyrogallol is soluble in less than three parts of cold water, and is still more soluble in hot. It is also freely soluble in alcohol and ether, but is not dissolved by absolute chloroform.

The acid properties of pyrogallol are very feebly marked. It is an active poison, producing symptoms similar to those occasioned by phosphorus.

---

[1] The true factor is 0·9126, the difference between this figure and 0·9 being a correction for a small quantity of cupric tannate dissolved by the ammonium carbonate.

[2] Often mis-stated as 115°–118° C.

Pyrogallol is permanent in dry air free from ammonia, but in moist or ammoniacal air it gradually darkens, and in aqueous solution it turns brown or black, especially when the liquid is heated. In presence of ammonia or fixed alkalies, it absorbs oxygen from the air with the greatest avidity, the liquid becoming brown, and ultimately almost black; the colour is destroyed by oxalic acid.

Fehling's copper solution, potassium ferricyanide, silver nitrate, and auric chloride are rapidly reduced by pyrogallol, and permanganate is decolorised in acid solutions with evolution of carbon dioxide.[1] With lime-water, or ammonia and calcium chloride, a fine purple colour is produced, rapidly changing to brown, but no precipitate is formed. This reaction is delicate and characteristic.[2] With ferrous sulphate a blue solution is formed, rapidly changing to green and red, and with ferric chloride a red coloration is given, turning brown when heated. Pyrogallic acid does not precipitate a solution of gelatin. The aqueous solution of pyrogallol is turned brown by nitrous acid. The reaction is very delicate.

---

[1] The oxidation of pyrogallol in acid or neutral solutions results in the formation of purpurogallol or purpurogallin, a body of the formula $C_{20}H_{16}O_9$ or $C_{18}H_{14}O_9$. It is most readily obtained by treating a solution of 20 parts of pyrogallol in 330 of water with a solution of 87 parts of potassium ferricyanide in 330 of water. Gas is evolved, the solution loses its deep red colour, and purpurogallin separates, the oxidation being complete in about half an hour. Purpurogallin crystallises from alcohol in brown velvet-like needles, melting at 156°, and volatilising at 200° with partial decomposition. It dissolves with difficulty in water, but readily in alcohol and ether, and is soluble in alkalies to form unstable blue compounds. The sodium salt contains Na_4, and gives with barium chloride an almost insoluble precipitate of the barium compound. In strong sulphuric acid, purpurogallin dissolves to a liquid which gives an intense violet coloration when a trace of nitrous acid or a nitrite is added. The colour is fugitive, but the reaction is said to be delicate and characteristic.

[2] For examining the behaviour of pyrogallic acid with lime-water, it is convenient to employ a nitrometer. This should be filled with mercury, or a recently boiled saturated solution of common salt, which has been previously treated with ammonium oxalate and filtered from any precipitate. A few cubic centimetres of the solution to be tested for pyrogallol is then allowed to enter through the tap, and the cup is rinsed with water, which is allowed to enter in its turn. Ammonia is next permitted to enter, when a slight brown coloration is usually produced owing to dissolved oxygen. On now allowing lime-water or calcium chloride to enter, a fine but rapidly fading purple colour will be developed, and this will be enormously intensified on admitting air and agitating the tube; in fact, in the entire absence of oxygen, the blue colour would probably not be produced. In the absence of calcium (or barium) compounds only a brown colour is produced on admitting air. Addition of potassium ferricyanide to the ammoniacal liquid produces an immediate dark brown coloration, apparently owing to the formation of the same oxidation-product as is produced by admitting air; but ferricyanide prevents the blue reaction with calcium salts, probably by immediately forming the more highly oxidised brown product.

Pyrogallic acid might probably be determined by titration in acid solution with standard permanganate, or perhaps by means of Fehling's solution. A process of determination might probably be based on the observation of the volume of oxygen absorbed by a solution of the substance after adding alkali.

Pyrogallic Ethers.

The volatile fractions of crude wood-tar creosote contain the dimethyl ethers of pyrogallol, methyl-pyrogallol, and propyl-pyrogallol (vol. ii. page 565). Heated with hydrochloric acid under pressure, these yield pyrogallol and its homologues. *Methyl-pyrogallol*, $C_6H_2(CH)_3(OH)_3$, resembles pyrogallol, melts at 129°, and volatilises unchanged. *Propyl-pyrogallol*, $C_6H_2(C_3H_7)(OH)_3$, is very soluble in water, alcohol, and ether, and melts at 79°–80°.

The pyrogallic ethers derive their chief interest from the remarkable colouring matters (originally discovered. by Runge), which can be derived from them by oxidation (*Pharm. Jour.*, [3], xii. 261, 428; *Jour. Soc. Chem. Ind.*, iv. 152).[1]

---

[1] Thus, if the sodium-derivative of dimethyl pyrogallate (prepared by adding soda to its alcoholic solution) be mixed with the sodium-derivative of dimethyl methyl-pyrogallate and excess of soda, and heated in the air, a body called eupittonic acid is formed:—$2C_8H_{10}O_3 + C_9H_{12}O_3 + O_3 = C_{25}H_{26}O_9 + 3H_2O$. On treating the mass with water, it dissolves with indigo-blue colour, which changes to carmine-red when the liquid is acidified. After removing impurities by shaking the acidulated solution with ether, the eupittonic acid may be extracted by agitation with boiling benzene. Eupittonic acid is a sparingly soluble body which crystallises from alcohol or dilute acetic acid in orange needles. It dissolves in ammonia with blue, and in the fixed alkalies with purple colour. On adding caustic soda to the orange solution of eupittonic acid in alcohol, a beautiful blue coloration is produced, and a flocculent precipitate is formed which gradually changes to a mass of small blue prisms having a beetle-green lustre, and consisting of sodium eupittonate, $C_{25}H_{24}Na_2O_9$. This compound is soluble in pure water, but the solution is precipitated by contact with air, and more rapidly by passing carbonic acid, and a blue precipitate is also thrown down by addition of brine. The eupittonates of calcium, magnesium, barium, tin, and other metals may be obtained as precipitates by double decomposition. The first two salts are soluble in pure water, the barium compound is a precipitate consisting of blue needles, while the lead salt crystallises in pale reddish needles. Reichenbach's "pittacal," called by Wichelhaus "eupittone," was a salt of eupittonic acid.

Eupittonic acid has the constitution of a hexamethoxyl-aurin,

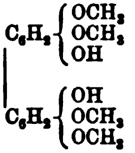
Galleïn, $C_{20}H_{10}O_7$, the phthaleïn of pyrogallol, is obtained by heating pyrogallol or gallic acid with phthalic anhydride to 190°–200°. It forms a brown-red powder, or beetle-green crystals which are almost insoluble in water, but soluble in alcohol. It is a weak acid, forming with alkalies a blue solution, becoming dirty coloured on standing. In ammonia, galleïn dissolves with violet colour, and the solution gives violet precipitates with metallic salts.

When heated to 200° C. with twenty times its weight of strong sulphuric acid, galleïn loses the elements of water, and is converted into

Cœruleïn, $C_{20}H_8O_6$, which on pouring the cooled solution into water is obtained as an amorphous black precipitate. It is nearly insoluble in water (which it colours olive-brown), alcohol, and ether, but dissolves easily in acetic acid. In commerce, cœruleïn occurs as a thick, dark-coloured paste. In alkalies it dissolves with beautiful grass-green colour, and the solution gives with mordants very stable lakes. With strong sulphuric acid cœruleïn gives a dirty brown colour. On warming cœruleïn with ammonia $C_{19}H_6(OCH_3)_6O_3$, and by heating with ammonia is converted into hexamethoxyl-pararosaniline, $C_{19}H_{10}(OCH_3)_6N_3$, which dyes silk, sulphurated wool, and tannated cotton a fine and pure blue.

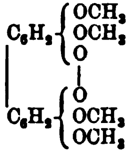
On subjecting the pyrogallic ethers from wood-tar creosote to more powerful oxidising agents than atmospheric air, such as dilute chromic acid mixture, they are converted into quinones; thus, dimethyl pyrogallate yields cœrulignone, $C_{16}H_{16}O_6$, a body which is identical with Reichenbach's "cedriret." It may be conveniently prepared by adding potassium bichromate to an acetic solution of the fraction of wood-tar creosote distilling between 250° and 260° C., when the liquid becomes hot and is soon filled with needles, which appear red in transmitted and a beautiful steel-blue by reflected light. Cœrulignone is insoluble in ordinary solvents, but dissolves in strong sulphuric acid to form a solution of a fine corn-flower tint, the coloration being so intense that the merest trace of the substance may be thus recognised. In phenol it dissolves with red and in creosote with blue colour, and is precipitated in steel-blue needles on adding alcohol or ether to its solution. By reducing agents it is converted into colourless hydrocœrulignone, $C_{16}H_{18}O_6$, soluble in alcohol and benzene, and readily reconverted into cœrulignone by oxidising agents. Hydrocœrulignone has the constitution of a tetramethyl ether of hexahydroxy-diphenyl, into which it may be converted by heating with hydrochloric acid to 200°; while cœrulignone is the corresponding quinone, thus:—

Hydrocœrulignone.



$$\begin{array}{l} C_6H_2\left\{\begin{array}{l}OCH_3\\OCH_3\\OH\end{array}\right.\\ | \\ C_6H_2\left\{\begin{array}{l}OH\\OCH_3\\OCH_3\end{array}\right.\end{array}$$

Cœrulignone.



$$\begin{array}{l} C_6H_2\left\{\begin{array}{l}OCH_3\\OCH_3\\O\end{array}\right.\\ | \qquad | \\ C_6H_2\left\{\begin{array}{l}O\\OCH_3\\OCH_3\end{array}\right.\end{array}$$

and zinc powder, a brownish-red solution is formed, containing cœrulin, $C_{20}H_{10}O_6$. The solution is oxidised in the air, the original green colour being restored. It may be employed in dyeing in the same manner as an indigo-vat.

On treating cœruleïn paste with two molecules of sodium bisulphite, $NaHSO_3$, a colourless compound of the two bodies is formed, which can be removed from the unaltered cœruleïn by extracting with cold alcohol. The bisulphite compound of cœruleïn occurs in commerce as a black powder under the name of *Cœrulein S.* It dissolves in water with greenish-yellow colour, and the solution becomes deep green, and sulphurous acid is evolved. Acids and alkalies effect the same decomposition in the cold.

Cœruleïn and the bisulphite compound are used for dyeing and printing cotton fabrics, on which they produce various shades of green. The colour is not removed from the fibre by boiling soap or caustic alkalies, and is darkened by concentrated hydrochloric acid. The most characteristic reaction is that with a warm, acid solution of stannous chloride, which turns the fibre brownish-red, owing to the formation of cœrulin. On then washing with water, or preferably very dilute solution of bleaching powder, the original green colour is restored.

GALLOCYANIN, also known as *solid violet*, is obtained by heating gallic acid or tannin in alcoholic solution with nitro-dimethylaniline hydrochloride. It is a crystalline substance with a green metallic lustre, slightly soluble in water with violet coloration, and in alcohol and dilute acids with carmine-red colour. It readily dissolves in alkalies, and forms a series of salts which crystallise well, that with aniline forming small green crystals. Gallocyanin dissolves in strong sulphuric acid with blue colour, becoming a redder shade on dilution. It dyes silk and wool without a mordant, and forms a beautiful violet-black-lake with oxide of chromium, a fact that is now utilised in cotton dyeing.

APPENDIX TO THE AROMATIC ACIDS.

TANNINS OR TANNIC ACIDS.[1]

Under the name of Tannin or Tannic Acid are known, and to a great extent confused, a considerable number of vegetable acids having great analogy to each other, but possessing distinct individuality. The different varieties of tannin or tannic acid agree in the following general properties :—

---

[1] See footnote on page 107.

TANNIC ACIDS are compounds of carbon, hydrogen, and oxygen containing a benzene nucleus. They are amorphous or subcrystalline solids of astringent taste, not fusible or volatile, more or less soluble in water, and freely so in alcohol, or a mixture of alcohol and ether, and notably in ethyl acetate. They are nearly insoluble in dry ether, and quite so in chloroform, benzene, petroleum spirit, and carbon disulphide. The tannins are generally but little soluble in dilute sulphuric acid. Their aqueous solutions give blue-black or green colorations or precipitates with ferric salts, and are all precipitated by the acetates of lead and copper and by stannous chloride. Some tannins are precipitated by tartar-emetic and by mineral acids. In some cases the tannin combines with the base only, but in others, as when cupric acetate is employed, the salt enters into combination as a whole. With a solution of gelatin, the tannic acids give precipitates analogous to leather, quite insoluble in presence of excess of tannic acid, but not wholly insoluble in pure water. Tannic acids, or most of them, can be completely removed from their aqueous solutions by the introduction of skin or rasped hide. The tannic acids are also removed from solution by digestion with cupric or zinc oxide, and they reduce Fehling's solution on heating. A delicate reaction for tannins (first noticed by the author, and apparently general) is the deep red colour produced on treating a solution with potassium ferricyanide mixed with ammonia. Tannic acids give insoluble precipitates with many organic bases, the rosaniline and cinchonine precipitates being among the least soluble; but it is frequently observable that an alkaloid and a tannin which occur together in the same plant do not combine together to form an insoluble compound.

The most characteristic property of the tannins is the formation, by combination with gelatin and gelatin-forming tissues, of the insoluble compounds which constitute leather.

All natural tannins are powerful reducing agents, and exhibit a marked tendency to absorb oxygen, especially in alkaline solution. The oxidation-products are often strongly coloured.

Extraction of Tannins.

The different natural tannins exhibit such differences, in their chemical reactions and behaviour with solvents, that it is not possible to give a general rule for their extraction in a state of purity. The following notes indicate the nature of the methods to be pursued:—

The method of Pelouze for the preparation of gallotannic acid from gall-nuts is as follows:—The powdered substance is exhausted with ordinary ether containing alcohol and water. On standing, the liquid separates into two layers, the lower of which contains tolerably pure gallotannic acid, while the upper ethereal layer retains the gallic acid. The tannin obtained by separating and evaporating the lower layer may be further purified by dissolving it in water and adding to the solution twice its measure of ether, when three layers are formed, the lowest of which contains nearly pure gallotannic acid.

A more generally applicable process of extracting tannins is the following :—The finely divided substance is exhausted by treatment with rectified spirit, the solution filtered, and evaporated to a small bulk at as low a temperature as possible (preferably under diminished pressure). The extract is treated at once with a considerable proportion of cold water, the liquid filtered and fractionally precipitated with acetate of lead. The first and last fractions should be rejected, as they are usually contaminated with colouring matters and other foreign substances. The tannate of lead is washed as rapidly as possible, suspended in water, and decomposed by sulphuretted hydrogen. The filtrate is shaken with ether to remove gallic acid, separated from the ethereal layer, and evaporated in a partial vacuum to the consistence of a thin syrup. The remaining water should be removed by exposure over sulphuric acid at the ordinary temperature.

Many tannins (*e.g.*, sumach-tannin and ratanhia-tannin) may be purified by agitating with ether to remove gallic acid, saturating the concentrated aqueous solution with common salt, and agitating it with acetic ether, which removes the tannin.

Some tannins (*e.g.*, hop- and alder-tannin) are stated to be insoluble in water after isolation, the change being probably due to partial decomposition. When the presence of such tannins is anticipated, the lead precipitate should be suspended in alcohol instead of water, before decomposing it with sulphuretted hydrogen.

Many other vegetable bodies besides tannins are precipitable by lead acetate, but they are commonly insoluble in cold water.

It not unfrequently happens that a single plant contains two or more tannins. Thus both oak- and willow- bark contain a little gallotannic acid in addition to their own peculiar tannins; and myrabolanes and divi-divi contain both gallotannic and ellagitannic acids. The existence of several tannins may be detected in some cases by fractional precipitation with lead acetate, and in others by examining the products of the action of dilute acid. Thus, oak-red produced from quercitannic acid is not removed by agitating the liquid with ether, while the gallic acid produced from the co-existent gallotannic acid is dissolved by the same menstruum.

Constitution of Natural Tannins.

From the tanner's point of view, the natural tannins may be arranged in two great classes, namely, those which produce a "bloom," or fawn-coloured deposit, on leather, and those which do not. The tannins giving a bloom on leather give a blue-black coloration with ferric acetate, while the others afford a green colour with the same reagent. To the first of these classes belong the tannins of gall-nuts, myrabolanes, divi-divi, sumach, valonia, and oak-bark, while the second includes the tannins of catechu, hemlock, larch, ratanhia, mangrove, and all the varieties of mimosa. The production of the "bloom" is in most cases due to the formation of ellagic acid, $C_{14}H_8O_9$, a body allied to gallic acid, $C_7H_6O_5$, of which most of the tannins of the first group may be considered to be derivatives. The tannins of oak-bark and valonia are either mixtures of two distinct tannins or of anomalous character, for they yield both gallic acid and protocatechuic acid, $C_7H_6O_4$; while of all the tannins which give a green reaction with ferric acetate are derivatives of the latter of these acids. These again may be divided into tannins which yield acetic or some other fatty acid on fusion with potash, and those which yield phloroglucol, $C_6H_6O_3$.

It has been shown by H. Schiff that the ordinary tannin of galls (gallotannic acid) is in great part a glucoside, and that under the influence of dilute acids, or of a peculiar nitrogenous ferment called pectase, it splits up into glucose and gallic acid, thus:—$C_{34}H_{28}O_{22} + 4H_2O = C_6H_{12}O_6 + 4C_7H_6O_5$. Many other of the natural tannins also furnish glucose by the action of dilute acids, but in some cases the change occurs with much less facility than is usual with glucosides. Hence it has been suggested by Hlasiewetz that the tannins are not true glucosides, but bodies which would be more correctly regarded as gummides or dextrides,[1] and hence that the formation of glucose by the action of dilute acids is due merely to a secondary action on the gum or dextrin. Some of the natural tannins certainly yield no glucose by the action of dilute acid, and in other cases its formation is still an open question.

The arrangement of natural tannins into classes is therefore based on the products they yield:—(1) when heated alone, (2) when heated with dilute acid, and (3) when fused with caustic alkali. The characteristic products obtained by heating tannins alone are pyrogallol and catechol; by heating with dilute acids, glucose, gallic acid, ellagic acid, and insoluble amorphous anhydrides called phlobaphenes; and by fusion with caustic alkali, pyrogallol, protocatechuic acid, acetic acid, and phloroglucol.

---

[1] Valonia is liable to a natural fermentation (ropiness), in which large quantities of dextrin or some similar body precipitable by alcohol are formed.

In the table on next page the principal kinds of tannin are arranged according to the foregoing principles of classification.

Certain of the tannins give a blue or black coloration when mixed in solution with ferric salts, while others yield a green or greenish colour when similarly treated. Speaking generally, the tannins which are derived from gallic acid give a blue reaction, while those derived from protocatechuic acid afford a green colour.

The reaction with iron salts is best observed by adding to an aqueous solution of the tannin contained in a test-tube one or two drops of a dilute solution of ferric acetate. This may be extemporised by adding sodium acetate to a solution of ferric chloride. Excess of the reagent must be avoided, or its colour and oxidising action may lead to error. The coloration produced by ferric acetate having been observed, it is advisable to add an excess of ammonia, and note any change which may occur.

If ferric chloride be substituted for the acetate, the general results are the same, but in some instances a greenish coloration is produced by tannins which give a distinct blue reaction with ferric acetate, and are undoubted gallic acid derivatives. This is especially the case if the ferric chloride solution contains free acid. Hence the acetate is much to be preferred as a reagent for tannins. Other reactions of tannins are given on pages 102, 103.

The following is a description of the best methods of operating with a view to the formation and recognition of the decomposition-products obtained by the action of heat, dilute acids, and fusing potash on the different kinds of tannin.

Action of Heat on Tannins.

When a tannin which produces a "bloom" on leather (Class A) is cautiously heated to about 200° C., it is decomposed with volatilisation of pyrogallol in feathery crystals. On the other hand, the tannins which produce no bloom, but red deposits, give a somewhat similar reaction, but the sublimate consists of catechol. From oak-bark and valonia, which apparently contain a mixture of both kinds of tannin, and hence yield both bloom and red colouring matters, both catechol and pyrogallol are produced on heating.

In using the heating test for distinguishing the two classes of tannins, the temperature must be carefully regulated, or much loss

Tannin.	Source.	Formula.	Products on heating with Dilute Acid.	Products of dry Distillation.	Products on Fusion with Caustic Potash.	Reaction with Ferric Acetate.	Remarks.
Digallic acid, . .	Gall-nuts.	$C_{14}H_{10}O_9$.	Gallic acid only.	Pyrogallol.	Pyrogallol and carbonic acid.	Blue-black.	See page 87.
Gallotannic acid (Glucoside), . .	Gall-nuts.	$C_{34}H_{28}O_{22}$.	Gallic acid and glucose.	Pyrogallic and metagallic acids.	Pyrogallol and carbonic and glucic acids.	Blue-black.	See page 86.
Ellagitannic acid, .	Divi-divi; myrabolanes.	$C_{14}H_{10}O_{10}$.	Ellagic acid only.	Pyrogallol.	...	Nearly black.	See page 92.
Sumach-tannin, . .	Sumach leaves.	$C_{16}H_{14}O_{10}$.	Gallic acid.	Do.	...	Blue-black.	Possibly identical with gallotannic acid.
Pomegranate-tannin, .	Pomegranate rind.	...	Ellagic acid and glucose.	Do.	...	Blue-black.	...
Caffetannic acid, .	Coffee berries.	$C_{14}H_{16}O_7$.	Caffeic acid and glucose.	Catechol.	Protocatechuic- and acetic acids.	Green.	See page 98.
Cinchotannic acid, .	Cinchona-bark.	$C_{14}H_{16}O_9$.	China red and glucose.	Do.	Do. do.	Green.	Very soluble in ether, &c.; two varieties exist.
Fern-tannin, . .	Male-fern.	...	Filix-red and glucose.	Do.	Do. do	...	..
Maté-tannin, . .	Paraguay tea.	...	? and glucose.	...	...	...	...
Valonia-tannin, . .	Valonia.	...	Valonia red.	Catechol and Pyrogallol.	Protocatechuic and gallic acids.	Blue-black.	...
Quercitannic acid, .	Oak-bark; tea leaves.	$C_{19}H_{16}O_{10}$.?	Oak red.	Do.	Protocatechuic acid and phloroglucol.	Blue-black.	See page 93.
Ulmotannic acid, .	Elm-bark.	...	Elm red.	Do.	Do. do.	Dirty green.	Probably identical with oak-tannin.
Salitannic acid, . .	Willow-bark.	...	Phlobaphene.	Catechol.	Do. do.	Deep black.	...
Lingué-tannin, . .	*Laurus caustica.*	$C_{17}H_{17}O_9$.	Phlobaphene.	Do.	Do. do.	Green.	...
Hemlock-tannin, .	Hemlock.	$C_{20}H_{18}O_{10}$	Hemlock red.	Do.	Do. do	Green.	...
Catechu-tannic acid, .	Catechu.	$C_{38}H_{34}O_{15}$.	Catechin.	Do.	Do. do.	Greenish.	See page 96.
Kinotannic acid, .	Kino.	$C_{28}H_{21}O_{11}$.	Kino red.	Catechol and phenol.	Do. do.	Green.	Alcoholic solution gelatinises.
Ratanhia-tannin, .	Ratanhia.	...	Ratanhia red.	...	Do. do.	Green.	Does not precipitate tartar-emetic.
Chestnut-tannin, .	Horse-chestnut.	$C_{26}H_{24}O_{12}$.	Chestnut red.	...	Do. do.	Green.	Does not precipitate tartar-emetic.
Morintannic acid, .	Fustic.	$C_{13}H_{10}O_6$.	Rufimoric acid.	Catechol.	Do. do.	Greenish	Crystallisable; yellow.
Tormentil-tannin, .	Tormentilla.	...	Tormentil red.	...	Do. do.	Green.	...
Quebrachitannic acid,	*Quebracho lorentzii.*	...	Quebracho red.	Catechol.	Do. do.	Green.	Precipitates gelatin and albumin.
Alder-tannin. . .	Alder-bark.	$C_{27}H_{28}O_{11}$.	Alder red and glucose.	Do.	Phloroglucol and protocatechuic and acetic acids.	Dirty green.	Insoluble in water after extraction. Does not ppte. tartar-emetic.
Lupulo-tannic acid, .	Hops.	$C_{25}H_{24}O_{13}$.	Hop red and glucose.	Do.	Do. do.	Greenish.	See page 96.
Animal tannin, . .	Corn weevils.	$C_{28}H_{16}O_{16}$.	See page 95.	...	..	Blue-black.	See page 95.

will ensue and the recognition of the pyrogallol or catechol will be greatly complicated by the formation of metagallic acid and other secondary products. A better result is obtained by mixing the substance with several times its weight of sand or powdered pumice, and passing a stream of coal-gas or carbon dioxide through the retort, so as to carry the products quickly out of the heated space. A still better and more convenient plan is the following, based on an observation of T. E. Thorpe (*Chem. News*, xliii. 109):—About 1 gramme of the sample should be heated with 3 c.c. of pure glycerin to a temperature of 190° to 200° C. for twenty minutes. After cooling, the product is treated with about 20 c.c. of water, and the liquid shaken with an equal measure of ether without previous filtration. The ethereal layer, which contains the pyrogallol and catechol, is separated from the aqueous liquid, evaporated to dryness, and the residue dissolved in 50 c.c. of warm water. The filtered solution is divided into several portions which are respectively tested with lime-water, ferric chloride, and ferric acetate (see page 69). These reagents readily distinguish catechol from pyrogallol when unmixed, and will suffice for the recognition of the one in presence of not too large a proportion of the other. It must be remembered that the production of pyrogallol may have resulted from the presence of gallic acid in the original substance, if the tannin had not previously been purified therefrom in the manner indicated on page 76. Catechol, on the other hand, may be a product of the decomposition of catechin and other bodies allied to and associated with tannins, unless care has been taken to remove them previously. As a general rule, however, catechins and catechol-derivatives only occur in quantity with catechol-tannins, and the same is true of gallic acid with regard to pyrogallol.

The characters of pyrogallol and catechol have already been fully described (pages 65 and 70).

Action of Dilute Acids on Tannins.

As already stated, many tannins are resolved on heating with dilute acids into glucose, and either gallic acid, ellagic acid, or an amorphous, insoluble, red colouring matter or phlobaphene, according to the nature of the tannin. Other tannins yield these products without glucose being simultaneously formed. As a rule, the action of dilute acid on a tannin results in the formation, apart from glucose, of a single decomposition-product belonging to the aromatic series (*e.g.*, gallic acid, ellagic acid, phlobaphene, &c.), but in some cases two or more of such bodies are producible from a tannin of apparently homogeneous nature (page 79).

To ascertain whether a tannin yields glucose by hydrolysis, it should first be carefully freed from any admixture of ready-formed carbohydrates by precipitation with neutral lead acetate, or saturation of the aqueous solution with salt and removal of the tannin by agitation with acetic ether, in the manner indicated on page 76. The washed lead salt, or the tannin left on evaporating the acetic ether, is then heated to 100° C. for some hours, with dilute hydrochloric acid, in a sealed tube or firmly closed bottle. (Mere boiling with the dilute acid, replacing loss by evaporation, is sufficient in most cases, especially for qualitative purposes.) After cooling and opening the bottle, the mixture should be allowed to stand for some time in the cold, to observe whether any sparingly-soluble decomposition-product separates.[1] In such case, the precipitate should be filtered off, and any traces remaining in solution removed by agitating the filtrate first with acetic ether and then with ordinary ether. The aqueous liquid is boiled, neutralised with soda, precipitated with basic lead acetate (to remove any traces of tannin or colouring matters), the liquid again filtered, the excess of lead removed by dilute sulphuric acid, the filtered liquid again neutralised by soda, and heated to boiling with Fehling's solution, when a yellow or red precipitate of cuprous oxide will prove the presence of glucose.

The *precipitate* produced on cooling the product of the action of dilute acid on the tannin may consist of lead chloride (if the lead compound has been used), ellagic acid, or a phlobaphene. The lead chloride may be removed by washing with boiling water. If the residue has a pale yellow or fawn colour, and is but slightly soluble in cold alcohol, it probably consists of ellagic acid, which is soluble in ammonia and hot alcohol, and dissolves readily in strong nitric acid with intense crimson coloration. A red residue, readily soluble in cold alcohol, will consist of a phlobaphene, which will be reprecipitated on diluting the alcoholic solution with water, and may be further examined by fusion with caustic potash.

The *ethereal layer*, obtained by shaking the filtrate from the ellagic acid and phlobaphenes with ether and acetic ether, will contain gallic acid, if any has been produced by the treatment of the tannin with dilute acid. For its recognition the ethereal solution should be evaporated to dryness, the residue taken up with cold water, and the solution filtered. The filtrate will give a fine red coloration with potassium cyanide, if gallic acid has been produced. The reaction may be confirmed by treating another portion of the filtrate with an aqueous solution of picric acid, followed by ammonia, when a reddish coloration, changing to a fine green, will be produced if gallic acid be present.

---

[1] To prevent subsequent source of error, it is desirable to get rid of any ready-formed gallic acid, by repeatedly agitating the solution of the tannin with ether before precipitating with lead acetate

In many cases it is not necessary to employ so elaborate a process as the foregoing in order to distinguish the class to which a tannin belongs. It is frequently sufficient to boil the tannin or its infusion with dilute hydrochloric acid for some time, replacing the acid lost by evaporation. The solution is then diluted and allowed to cool, when ellagic acid and phlobaphenes will separate, and may be filtered off and separated by treatment with cold alcohol as already indicated.

Gallic acid has already been fully described. Ellagic acid is considered on page 92.

PHLOBAPHENES.

Chemically, the phlobaphenes are anhydrides of the respective tannic acids from which they are derived, or, in other words, they are formed from these tannins by the loss of one or more molecules of water. In this way they are produced by the action of dilute acids on tannins, and may also be formed in many cases by pouring alcoholic or highly concentrated aqueous solutions of the tannins into cold water, under which circumstances a part of the tannin seems unable to assimilate water and the phlobaphene separates as a red precipitate. Phlobaphenes exist ready-formed in most tanning materials capable of producing them, and may be dissolved out of these or the dried extracts thereof by means of alcohol.

The phlobaphenes are red or brown amorphous bodies, difficultly soluble in pure or acidulated water or in pure ether, but soluble in water containing ammonia, and freely soluble in spirit. Some phlobaphenes are so sparingly soluble in water, even when boiling, that the character may be utilised for the determination of the corresponding tannin. This is especially the case if, after heating with hydrochloric acid, the liquid be evaporated to dryness and the residue treated with water. The decomposition-products then often remain almost entirely undissolved, but not wholly so, for, though mostly insoluble in pure water, they are dissolved more or less by solutions of sugar and other substances. The phlobaphenes are also dissolved by dilute alkalies and alkaline carbonates, and by borax, which last substance is said to be used in the preparation of some tannin extracts, and has been suggested as a means of rendering phlobaphenes available for tanning. The solubility of the phlobaphenes in water depends much on their degree of hydration, many tannins giving a whole series of anhydrides, of which those containing only one molecule of water less than the original tannin are quite soluble in water, while the higher members of the series become less and less soluble as they lose water. The soluble phlobaphenes are the colouring matters of tanning materials, and behave like the tannins themselves, precipitating gelatin and combining with hide to form leather.[1]

In many cases (*e.g.*, gambier) it is certain, and in others it is probable, that the tannin itself is merely the first anhydride of the series, and is derived from a catechin which is itself white, crystallisable, and destitute of tanning properties.

The phlobaphenes somewhat resemble the resins in their analytical characters, as, for instance, their solubility in alcohol and slight solubility in water, and in their behaviour when fused with caustic alkali; but they are distinguished from the resins by dissolving in dilute ammonia. With gelatin, ferric acetate, and lead acetate the phlobaphenes usually react like their respective tannic acids. Occasionally a so-called tannin is met with (*e.g.*, hop-tannin), which is not precipitated by gelatin, while the phlobaphene therefrom is precipitated.

Phlobaphenes are yielded by the tannic acids from the bark of the oak, elm, horse-chestnut, willow, birch, fir, and acacia, as well as by the tannins from rhubarb, male-fern, wine, &c. According to Grabowski, the phlobaphenes from the tannins of the oak, ratanhia, and tormentilla are not merely analogous to but actually identical with chèstnut-red (see Quercitannic Acid, page 94).

Action of Fused Alkali on Tannins.

When tannins are subjected to the action of caustic alkali in a state of incipient fusion, they are broken up with formation of products varying with their constitution. Thus all the tannins yielding catechol on dry distillation, that is, all those which give a green colour with ferric acetate—and valonia and oak-bark tannins in addition—give protocatechuic acid when fused with caustic potash. On the other hand, those tannins which give pyrogallol when heated alone yield gallic or ellagic acid when fused with caustic alkali.[2] In each case the reaction consists in the elimination of CO_2.

---

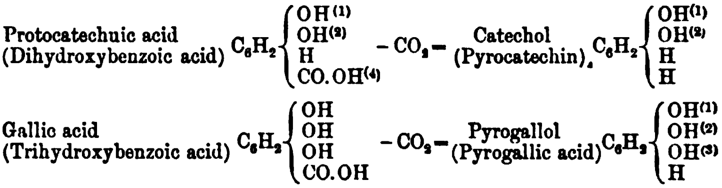
[1] Hemlock-bark yields a series of such bodies, of which the lower members are deep-red soluble tannins, and the higher form the red sediment which occurs in hemlock extract. It is not possible to decolorise hemlock extract without at the same time greatly reducing its tanning powers, though by preparing and concentrating it at a low temperature the proportion of insoluble higher anhydrides formed may be kept at a minimum.

[2] The relationship of these products of the decomposition of tannins is shown by the following formulæ:—

The tannins which yield protocatechuic acid on fusion with alkali may be further subdivided according to the secondary product formed simultaneously, one class giving acetic or some other fatty acid, and a second a body called phloroglucol (page 85).[1] A third class, including the tannins of the alder and hop, give both acetic acid and phloroglucol, but this peculiarity is not improbably due to the coexistence of two distinct tannins.[2] All those tannins which yield acetic acid instead of phloroglucol on fusion with potash give notable proportions of glucose on heating with dilute acid, while some, and probably all, of the phloroglucol-tannins give no sensible quantity of glucose.

To recognise the presence of a phloroglucol-tannin without employing the tedious method described on next page, H. R. Procter mixes 5 c.c. of water, 1 c.c. of a saturated solution of commercial nitrate of aniline, and 1 c.c. of a very dilute solution of potassium nitrite. To this liquid is added 1 c.c. of a solution containing as nearly as possible ½ per cent. of the tannin to be examined. If phloroglucin or a phloroglucide-tannin be present the liquid will gradually become yellow or orange, and will deposit a cinnabar-red precipitate after standing for a time not exceeding one hour, but many other bodies give precipitates which may lead to mistaken conclusions. Thus the reaction is produced by oak-bark infusion, which is not supposed to contain a phloroglucol-tannin, and gall-tannin, pyrogallol, and other substances give similar but browner precipitates. A sharper distinction may be obtained by employing more dilute solutions, but it is preferable, when possible, to act on the tannin with fusing potash and examine the products.

The fusion with potash may be conducted either on the original tannin or on the body produced by treating it with dilute acid, When convenient, the lead salt may be substituted for the free



$$\begin{array}{l}\text{Protocatechuic acid}\\\text{(Dihydroxybenzoic acid)}\end{array} C_6H_2\begin{cases}OH^{(1)}\\OH^{(2)}\\H\\CO.OH^{(4)}\end{cases} - CO_2 = \begin{array}{c}\text{Catechol}\\\text{(Pyrocatechin).}\end{array} C_6H_2\begin{cases}OH^{(1)}\\OH^{(2)}\\H\\H\end{cases}$$

$$\begin{array}{l}\text{Gallic acid}\\\text{(Trihydroxybenzoic acid)}\end{array} C_6H_2\begin{cases}OH\\OH\\OH\\CO.OH\end{cases} - CO_2 = \begin{array}{c}\text{Pyrogallol}\\\text{(Pyrogallic acid)}\end{array} C_6H_2\begin{cases}OH^{(1)}\\OH^{(2)}\\OH^{(3)}\\H\end{cases}$$

---

[1] The formation of these products is due to a reaction allied to saponification, thus :—

$$\underset{\substack{\text{Morintannic}\\\text{Acid.}}}{C_{13}H_{10}O_6} + KHO = \underset{\substack{\text{Potassium}\\\text{Protocatechuate.}}}{KC_7H_5O_4} + \underset{\substack{\text{Phloro-}\\\text{glucol.}}}{C_6H_6O_3}.$$

[2] The fusion of gallic acid with caustic soda is said to result in the formation of a small quantity of phloroglucol (*Jour. Chem. Soc.*, xliv. 60).

tannic acid. The separation or recognition of protocatechuic and gallic or pyrogallic acids when mixed is very troublesome, and hence it appears better in most cases simply to aim at the isolation and recognition of phloroglucol. The following is the method usually prescribed for this purpose:—20 grammes of the tannin, phlobaphene, or lead salt is boiled with 150 c.c. of solution of caustic potash, of 1·2 specific gravity, for two or three hours, and the liquid then concentrated with continual stirring till it becomes pasty, the alkali undergoing fusion.[1] The product is cooled, and treated with dilute sulphuric acid in quantity sufficient to render the whole distinctly acid when cold, the liquid is filtered from the potassium sulphate and other solid matters, and the filtrate is treated with sodium bicarbonate till its wine-red reaction with litmus (or absence of red coloration with methyl-orange) shows that the sulphuric acid is neutralised. The liquid is then shaken several times with ether, and the ethereal solution evaporated. The residue contains phloroglucol, recognisable by its sweet taste and reactions with ferric chloride and fir-wood. If necessary, it may be purified from protocatechuic acid by precipitating the aqueous solution with neutral lead acetate, the filtrate being extracted with ether, or evaporated after separating the excess of lead by sulphuretted hydrogen.

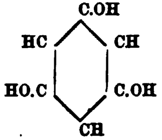
Phloroglucol. Phloroglucin. $C_6H_6O_3$. This substance is isomeric with pyrogallol and hydroxyquinol, and is generally regarded as symmetrical trihydroxybenzene, but there is evidence in favour of a different constitution.[2] It is possible that it exists in both forms, one of which is readily converted into the other. Phloroglucol forms small plates or rhombic tablets containing 2 aqua. It becomes anhydrous at 100°, and melts at 218° if heated rapidly, but at 209° or even 200° if slowly heated. At a higher temperature it sublimes without odour, and solidifies again on cooling.

Phloroglucol is sweeter than cane-sugar. It is soluble in water and alcohol, and readily in ether, and by agitation with the last solvent can be removed from its aqueous solution. An aqueous

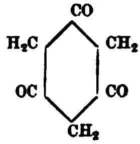
---

[1] In some cases, such as that of phloretin, it is sufficient to boil the substance with caustic potash solution, as described in the text, omitting the subsequent evaporation and fusion.

[2] Symmetrical Trihydroxybenzene.



Modified Formula of Phloroglucol.



solution of phloroglucin is not precipitated by any metallic salt except basic lead acetate. It is coloured deep violet by ferric chloride, and reduces Fehling's solution and ammonio-nitrate of silver. In concentrated aqueous solution it is converted by bromine into tribromo-phloroglucol, $C_6H_3Br_3O_3$, which immediately separates in long needles, the liquid emitting a powerful, tear-exciting odour.

When dilute solutions of phloroglucol and nitrate of toluidine or aniline are mixed, and a very dilute solution of potassium nitrite added, the liquid gradually becomes turbid and of a brownish-yellow colour, then orange-red, and finally a vermilion-red precipitate is produced. The reaction is extremely delicate.

If a freshly-cut slip of deal be moistened with a dilute solution of phloroglucol (½ per cent.), and subsequently with dilute hydrochloric acid, it acquires an intense violet or red colour. The reaction is very delicate.[1]

Gallotannic Acid. Tannic Acid. Tannin.

Gallotannic acid occurs in gall-nuts in proportions commonly ranging from 60 to 77 per cent., and is usually prepared therefrom by the method of Pelouze described on page 75.[2]

A preferable and more modern plan is to extract gall-nuts with a mixture of 12 parts of ether and 3 of alcohol, 12 parts of water being added to the extract, and the alcohol and ether removed by distillation. The residual aqueous solution is then filtered and evaporated, the product being further purified by solution in water and treatment with animal charcoal.

Pure gallotannic acid may also be obtained, according to Schiff, by extracting gall-nuts with anhydrous ether to which 5 per cent. of alcohol has been added.

As prepared by Pelouze's process, tannin yields more or less glucose or an analogous body when treated with dilute acids (the amount obtained varying from 0 to 22 per cent.), gallic acid being formed at the same time. Hence ordinary tannin is commonly regarded as a glucoside of gallic acid and represented by the empirical formula $C_{34}H_{28}O_{22}$, which would yield 23 per cent. of glucose on hydrolysis. As prepared by Schiff's process, however, gallotannic acid yields little or no glucose on treatment with dilute acid, and hence is not a glucoside, though agreeing in its other characters with the product obtained by Pelouze's method. It appears probable, therefore, that the latter contained an admixture of actual glucose, or of a glucoside brought into solution by the water present, just as oak-bark tannin is liable to contamination by lævulin or the lævulose formed therefrom.

---

[1] The coloration is readily obtained with infusion of gambier and probably of other phloroglucol tannins, but is also given by catechol (page 65).

[2] A further purification may be effected by fractionally precipitating the aqueous solution of the product by acetate of lead, the first and last fractions being rejected. The lead tannate is then treated with a quantity of solution of oxalic acid insufficient for its complete decomposition, and the liquid filtered and evaporated, first at 100° C. and subsequently *in vacuo*.

H. Schiff has obtained gallotannic acid synthetically by drying gallic acid at 110°, mixing it into a thin paste with phosphorus oxychloride, and heating the mixture first to 100° and then to 120° C. Much hydrochloric acid is evolved, and the gallic acid is converted into a yellow powder, which should be washed with ether and dissolved in water. The unchanged gallic acid is allowed to crystallise out, after which the solution is saturated with common salt, the precipitated tannin is washed with brine and redissolved in ether alcohol. The product thus obtained gives all the reactions of purified gall-tannin, but is perfectly reconverted into gallic acid on boiling with hydrochloric acid, without the formation of any trace of glucose or ellagic acid.

It may now be considered fully established that pure gallotannic acid or tannin from galls has the composition $C_{14}H_{10}O_9$, and in constitution is the first anhydride of gallic acid, or digallic acid. Its relation to gallic acid and some other allied bodies is shown by the following formulæ :—

Gallic acid. Trihydroxybenzoic acid,	$CO\left\{\begin{array}{l}C_6H_2(OH)_3\\OH.\end{array}\right.$
Gallotannic acid. Digallic acid,	$CO\left\{\begin{array}{l}C_6H_2(OH)_3\\O.C_6H_2(OH)_2.COOH.\end{array}\right.$
Ellagitannic acid, ...	$CO\left\{\begin{array}{l}O.C_6H_2(OH)_3\\O.C_6H_2(OH)_2.COOH.\end{array}\right.$
Ellagic acid, ...	$CO\left\{\begin{array}{l}O.C_6H_2(OH)_2—O\\O.C_6H_2(OH)\angle COOH.\end{array}\right.$
Sumach-tannin, ...	$CO\left\{\begin{array}{l}C_6H_3(OH)_3\\O.C_6H_2(OCH_3)_2.COOH.\end{array}\right.$
Kinoïn, ...	$CO\left\{\begin{array}{l}C_6H_2(OH)_3\\O.C_6H_4(OCH_3).\end{array}\right.$
Protocatechuic acid, . . .	$CO\left\{\begin{array}{l}C_6H_3(OH)_2\\OH.\end{array}\right.$
Quercitannic acid (?), . .	$CO\left\{\begin{array}{l}C_6H_3(OCH_3)_2\\O.C_6H_2(OH)(OCH_3).COOH.\end{array}\right.$

The foregoing formula for gallotannic acid explains satisfactorily the following reactions:—

1. The formation of gallic acid by hydrolysis:—$C_{14}H_{10}O_9 + H_2O = 2C_7H_6O_5$.

2. The formation of gallamide and ammonium gallate in almost theoretical proportions by boiling gallotannic acid with aqueous ammonia in an atmosphere of hydrogen:—

$$\begin{aligned} &C_6H_2(OH)_3.CO.O.C_6H_2(OH)_2.CO_2H + 2NH_3 \\ &= C_6H_2(OH)_3.CO.NH_2 + C_6H_2(OH)_3.CO_2.NH_4. \end{aligned}$$

3. The formation of a pent-acetyl-derivative by boiling tannin with acetic anhydride for one hour, the five hydroxyl groups being replaced by a corresponding number of C_2H_3O groups.

4. The formation of tannin, or a body giving all its reactions, by heating monobromo-protocatechuic acid with potassium gallate and alcohol:—$C_6H_2(OH)_3.COOK + BrC_6H_2(OH)_2.COOH = KBr + C_6H_2(OH)_3.CO.O.C_6H_2(OH)_2.COOH$.

Pure gallotannic acid forms a colourless amorphous mass, light yellowish buff-coloured scales, or brittle vitreous masses. It becomes yellow in the light even if air be excluded. The taste is strongly astringent, and the reaction acid. When heated it darkens with or without fusing, and at 215° decomposes with volatilisation of water, pyrogallol, and carbon dioxide, while a residue of metagallic or melanogallic acid, $C_6H_4O_2$, is left. This last substance is the sole product when tannin is rapidly heated to 280°, and is a black, amorphous, tasteless mass.

Gallotannic acid is soluble in 6 parts of cold water, and more readily in hot. It is precipitated from its concentrated solution by dilute hydrochloric or sulphuric acid, common salt, and potassium chloride and acetate, but not by sodium sulphate or nitric acid. Skin and other gelatinous tissues remove it completely from its aqueous solution.

In absolute alcohol gallotannic acid only dissolves sparingly, but it is soluble with great facility in hydrous alcohol. In absolutely dry ether free from alcohol tannin is almost insoluble, but if water be gradually added the tannin first coagulates and then deliquesces, and after a certain proportion of water has been added the liquid separates into three layers. This happens when 100 grammes of tannin is treated with 150 c.c. of ether, and 100 c.c. of water added. The lowest layer is a concentrated aqueous solution of tannin; the middle layer contains some tannin and much water; while the uppermost layer consists of ether holding a little tannic acid in solution.

Gallotannic acid is practicably insoluble in chloroform, benzene, petroleum ether, and carbon disulphide. In acetic ether and in glycerin it dissolves readily.

When taken internally gallotannic acid appears to be converted into gallic acid, which may afterwards be found in the blood and urine. Tannin diffuses but slowly in aqueous solution, but may be dialysed from its solution in alcohol.

Gallotannic acid is readily oxidisable. It reduces the salts of gold, silver, mercury and copper, permanganates, &c. Nitric acid rapidly oxidises it, with formation of oxalic acid; and chlorine, bromine, iodine, and chromic acid act violently.

Gallotannic acid decomposes carbonates and acts as a monobasic acid. Its solution in caustic alkali rapidly oxidises, and acquires a brown colour. The gallotannates are amorphous and difficult to prepare pure. Most of them are insoluble.

One of the most important and characteristic reactions of gallotannic acid is the formation of a white (or buff-coloured) flocculent precipitate with a solution of gelatin. The precipitate, which is the basis of leather, and is sometimes called tannate of gelatin, is not completely insoluble in pure water, but is wholly insoluble in presence of excess of tannic acid. When freshly formed it is often extremely finely divided, and passes through the closest filter, but becomes coagulated by adding ammonium chloride, alum, and certain other neutral salts.

Added to a dilute solution of gallotannic acid, ferrous sulphate occasions no change, if free from ferric salt, but produces a white precipitate in a concentrated solution. With ferric chloride tannin produces a bluish-black precipitate of ferric gallotannate (ink), the colour of which is destroyed by boiling or reducing agents. Addition of hydrochloric acid in excess dissolves the precipitate, which is reproduced on adding sodium acetate. Ferric acetate behaves like ferric chloride.

Gallotannic acid gives no reaction with a solution of cupric sulphate, but on adding excess of ammonia it is completely precipitated. The reaction may be employed for its determination. Fehling's solution is reduced by gallotannic acid on heating.

With tartar emetic and soluble salts of lead and bismuth, gallotannic acid yields white insoluble precipitates. With lime-water and with ammoniacal barium chloride it yields a white precipitate, turning blue on exposure.

Gallotannic acid is not precipitated by calcium acetate from a solution very slightly acidulated with acetic acid, and the liquid remains clear even after adding twice its volume of alcohol (separation from tartrates, citrates, oxalates, malates, &c.).

With an ammoniacal solution of potassium ferricyanide, gallotannic acid produces a deep red colour changing to brown, even in very dilute solutions. The reaction, which was first observed by the author, is very delicate, but the colour is destroyed by a large excess of the reagent. A somewhat similar reaction is produced by gallic acid.

Ammonium molybdate yields with tannin a red coloration, which is yellow in very dilute solutions, and is destroyed on adding oxalic acid.

Gallotannic acid may be determined with considerable accuracy by oxidation with a standard solution of permanganate (page 109).

Gallotannic acid may be extracted from its acidulated aqueous solutions by repeatedly agitating with ethyl acetate free from alcohol, and may thus be separated from tartaric, citric, malic, and other vegetable acids, but not from gallic acid. In the case of ink, sufficient oxalic acid must be added wholly to change the colour of the liquid.

Some of the foregoing reactions furnish important distinctions between gallotannic acid and gallic acid and pyrogallol, which in many respects it closely resembles. Others seem to distinguish it from the different varieties of tannin. The table on page 69 shows the reactions of gallotannic and gallic acids and pyrogallol in juxtaposition. The comparative reactions of gallotannic acid and other tannins are given on pages 102, 103.

COMMERCIAL GALLOTANNIC ACID is often far from pure. It frequently contains more or less glucose, chlorophyll, volatile oil, and gallic and ellagic acids. Starch has been met with to the extent of 25 per cent., and in more than one instance the author has known it to be entirely substituted by gallic acid, either intentionally or accidentally.

Glucose may be detected by precipitating the solution of the sample with basic acetate of lead, and heating the filtrate with Fehling's solution. A *glucoside* may be detected by the same method, after boiling the solution with dilute sulphuric acid for ten minutes, and neutralising the liquid with soda.[1]

If *chlorophyll* be present, on shaking the sample with an equal weight of water and the same volume of ether the ethereal layer will be coloured more or less greenish.

---

[1] According to J. E. Saul (*Pharm. Jour.*, [3], xvii. 387), a very delicate test for glucose, by which it can usually be detected in samples of commercial tannin, is to agitate about 0·01 gramme of the sample with 3 c.c. water, and then add three drops of an alcoholic solution of thymol. 3 c.c. of concentrated sulphuric acid should then be poured in so as to form a separate layer below the aqueous liquid. Under these circumstances, tannin containing sugar yields a turbid deep rose-coloured solution, while gallic acid remains untinted, or merely develops a very faint pink tint in the sulphuric acid layer; and pyrogallol yields a dull violet solution.

Gallotannic acid should be wholly soluble in alcohol. If a residue be left it should be examined for *starch*.

Mineral impurities will be indicated by ignition. As a rule, commercial tannin leaves a very insignificant proportion of ash, 0·4 per cent. being apparently the maximum proportion recorded.

Gallic acid may be detected in commercial tannin by leaving the aqueous solution of the sample in contact with a piece of untanned skin, and agitating the liquid from time to time. If the tannin be pure it is entirely absorbed, and the liquid becomes insipid, and no longer gives a coloration with ferric chloride; the contrary being the case if gallic acid be present.

A test which is said to be shorter than the above, and at the same time capable of detecting traces of gallic acid in tannin, has been described by S. Young (*Chem. News*, xlviii. 31). The sample is dissolved in a little water, ether added equal in measure to about one-third of the water used, and the whole well shaken. On standing, three layers are formed. The ethereal or uppermost is removed, evaporated, and the residue dissolved in water and tested with potassium cyanide, when a strong red coloration will be obtained if the sample contained even a trace of gallic acid. The middle layer contains still more gallic acid, while the lowest aqueous layer is almost free from it. By repeating the agitation with ether several times a complete separation of the gallic acid can be effected.

A determination of the actual *gallotannic acid* present in the commercial article is best made by Löwenthal's permanganate method. The residue of "not tannin" does not appear always to consist entirely of gallic acid, glucose being probably present in some cases.[1] The following results were obtained by T. Maben (*Pharm. Jour.*, [3], xv. 852), by applying Löwenthal's method to representative specimens of commercial tannin. The *moisture* was determined by drying the samples *in vacuo* over sulphuric acid.[2]

---

[1] The author found that commercial tannin varied to the extent of 30 to 40 per cent. in its power of precipitating acetate of lead, which would react with both gallic and gallotannic acids.

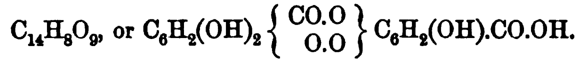
[2] According to C. Böttinger (*Jour. Soc. Dyers*, &c., July 1888), even the purest commercial tannin is not a uniform substance. When heated to 150°, under pressure, with concentrated hydrochloric acid, it gives off a gas burning with a green-edged flame (methyl chloride); and on heating the tannin with water and excess of bromine, small quantities of products volatile with steam are produced. Nevertheless such tannin is almost completely fixed by hide, and yields nothing but gallic acid when boiled with aqueous caustic alkalies. When boiled with a mixture of phenylhydrazine hydrochloride and sodium

	1	2	3	4	5	6	7	8	9
Moisture, ...	5·0	8·0	5·0	7·0	6·0	7·0	3·0	3·0	4·0
Gallotannic acid, . .	88·8	86·9	54·4	56·9	79·9	77·2	82·3	59·7	70·7
Not-tannin (by difference),	6·2	5·1	40·6	36·1	14·1	15·8	14·3	37·3	25·3
$KMnO_4$ required for "not tannin,"	5·86	1·92	6·01	6·94	1·08	3·08	6·63	5·55	3·39

Ellagitannic Acid. $C_{14}H_{10}O_{10}$.

This variety of tannin is contained in divi-divi and myrabolanes, and as a glucoside in pomegranate rind. When boiled with dilute acids, or heated with water to 110° C. in a sealed tube, it loses H_2O and yields the anhydride, ellagic acid. In its other chemical reactions, ellagitannic closely resembles gallotannic acid, but yields a light brown precipitate with cupric acetate.

ELLAGIC ACID.



$$C_{14}H_8O_9,\ \text{or}\ C_6H_2(OH)_2\left\{\begin{matrix}CO.O\\O.O\end{matrix}\right\}C_6H_2(OH).CO.OH.$$

This acid differs in composition from gallotannic acid by two atoms of hydrogen, and is formed when a concentrated aqueous solution of that body is exposed for a considerable time to the air, or by its reaction with iodine:—$C_{14}H_{10}O_9 + I_2 = 2HI + C_{14}H_8O_9$. Ellagic acid is also produced by the dehydration of ellagitannic acid (see above), and by the action of oxidising agents on gallic acid. It is a constituent of bezoar stones.[1] Air-dried ellagic acid contains 1 molecule of water, which it loses at 100° and re-absorbs in moist air. When heated to 200° C. it loses H_2O, and forms an anhydride, $C_{14}H_6O_8$, which is slowly reconverted into ellagic acid by boiling with water. When pure, ellagic acid forms a sulphur-yellow crystalline substance, nearly insoluble in water, even when boiling, and but little soluble in alcohol. The aqueous and alcoholic solutions have an acid reaction. It is but slightly soluble in ether, but small quantities may be effectually extracted from the aqueous solution by agitation with that solvent. In

acetate it becomes intensely yellow, changing to a brownish-yellow coagulated mass on standing. This reaction is not caused by the presence of a sugar.

[1] Ellagic acid is readily prepared by pouring a concentrated alcoholic extract of divi-divi into water. The precipitate may be purified by crystallisation from hot alcohol. It may also be obtained by boiling the aqueous extracts of divi-divi, myrabolanes, pomegranate rind, &c., with dilute hydrochloric acid, and may be purified by solution in alcohol. It may also be prepared by heating gallic acid with dry arsenic acid to 160° C., but the product is difficult to purify from arsenic. It may be obtained from bezoar stones (intestinal concretions of a Persian species of goat) by boiling with potash and precipitating with hydrochloric acid.

caustic potash ellagic acid dissolves with yellow colour, which rapidly becomes darker, and black crystals of potassium glaucomelanate separate. Neutral ferric chloride, when shaken with solid ellagic acid, is coloured greenish at first, but afterwards becomes inky black. The solution of ellagic acid in hot alcohol has a pale yellow colour, and deposits the acid in sulphur-yellow crystals on cooling. With lead acetate ellagic acid yields a precipitate containing 63 per cent. of PbO. Ellagic acid dissolves in fuming nitric acid with deep crimson coloration. With the product from divi-divi, the nitric acid solution retains its crimson colour on dilution with water, but when derived from other sources, dilution is said to change the colour to orange.

Caffetannic Acid. Caffetannin. $C_{14}H_{16}O_7$.

This variety of tannic acid occurs in coffee berries. When isolated it forms brittle masses or a yellowish-white powder. It is only slightly soluble in ether. On boiling caffetannic acid with dilute sulphuric acid, or by exposing its solution in caustic alkali to the air, the liquid acquires a bluish-green colour owing to the formation of the oxidation-product viridic acid. This body is characterised by giving a blue precipitate with lead acetate, and a crimson colour with strong sulphuric acid. On prolonged boiling with caustic alkalies, caffetannic acid yields caffeic acid, $C_9H_8O_4$, which crystallises from the neutralised solution. When fused with caustic potash, caffetannic acid yields protocatechuic and acetic acids. Heated alone, it gives catechol. Ferric chloride gives a dark green colour with caffetannic acid, and cinchonine sulphate a white precipitate, but solution of gelatin is not affected.

Quercitannic Acid. Quercitannin.[1]

According to C. Etti (*Jour. Chem. Soc.*, xliv. 994) the tannin of oak-bark exists in two forms, namely, as quercitannic acid, and as an anhydride of that acid, or phlobaphene.[2]

---

[1] Quercitannic acid is said to be identical with the tannins of the elm, willow, and black tea.

[2] Quercitannic acid may be prepared from treating oak-bark with alcohol, evaporating the filtered liquid, dissolving the extract in water, and agitating the solution with acetic ether. The product obtained on separating and evaporating the ethereal layer is contaminated by a brownish-green terpene resin and with some of the anhydrides of the tannin. The resin may be removed by treating the dried extract with ether or benzene, in which it is readily soluble; and the phlobaphenes or tannin-anhydrides may be separated by dissolving the tannin in ether-alcohol, or partially by mere solution in cold water. Or the soluble anhydrides may be precipitated by saturating the aqueous solution of the alcoholic extract with common salt before shaking with acetic ether.

Quercitannic acid is not a glucoside, the reactions which formerly caused confusion being really due to the presence of lævulin, which on treating the oak-bark with dilute sulphuric acid was converted into lævulose.

Quercitannic acid is amorphous, brownish-red, and readily soluble in water and alcohol. When pure, it dissolves completely in ethyl acetate, and does not yield anything to pure ether or benzene.

In very dilute alcoholic solution, quercitannic acid yields a pure yellow precipitate with neutral or basic acetate of lead, but in aqueous solution the precipitate produced is light brown. With ferric and ferroso-ferric salts quercitannic acid gives a blue-black colour, and yellowish-white precipitates with tartar-emetic, gelatin, albumin, and alkaloids. It is also precipitated by solution of lead nitrate, ammoniacal chlorides of zinc and magnesium, ammoniacal sulphate and acetate of copper, and by molybdate of ammonium. It readily reduces permanganate and Fehling's solution. According to H. R. Procter, a dilute solution of quercitannic acid does not precipitate blood-albumin, and in addition renders it uncoagulable by heat, even in presence of free acid.

According to Etti, quercitannic acid has the composition $C_{17}H_{16}O_9$.[1] At 130° to 140° it gives up water and yields the first anhydride or phlobaphene, $C_{34}H_{30}O_{17}$, which is brownish-red, nearly insoluble in water and in ether, but readily soluble in alcohol of all strengths. It exists in the original bark together with quercitannic acid, and gives a brownish-red precipitate with lead acetate. When boiled with dilute sulphuric or hydrochloric acid, the phlobaphene loses 1 molecule of water and yields a second anhydride, $C_{34}H_{28}O_{16}$, from which a third, $C_{34}H_{26}O_{15}$, may be obtained. All these anhydrides are soluble in alcohol and caustic alkalies, and are precipitated blue-black by ferric chloride. Löwe has obtained a fourth anhydride, $C_{34}H_{24}O_{14}$, which he designates oak-bark red, a name which has been applied by other observers to the first and second anhydrides.

Tanners designate the anhydrides simply as "colouring matter," and reject barks containing a large proportion, as they impart too red a colour to the leather.

---

[1] Etti points out the following distinctions between gallotannic and quercitannic acids:—

	Gallotannic Acid	*Quercitannic Acid*
Heated with dilute sulphuric acid to 140° under pressure,	Yields gallic acid, giving a white precipitate with lead acetate.	Yields phlobaphene or oak-red, giving a brown precipitate with lead acetate.
Heated with acetic anhydride,	Forms aceto-tannins.	Yields anhydrides and acetylised anhydrides.
Boiled with aqueous ammonia in an atmosphere of hydrogen.	Yields gallamide and ammonium gallate.	Yields indefinite resinous products.

From the number and mode of formation of these anhydrides, together with the evolution of methyl chloride on heating the tannin under pressure with dilute hydrochloric acid, Etti concludes that quercitannic acid is a methyl-derivative of digallic or gallylgallic acid. Etti also investigated a tannic acid of the formula $C_{20}H_{20}O_9$, obtained from the bark of a different species of oak. This agreed with the other acid in all its properties, except that it gave a bluish-green colour with ferric chloride, rapidly changing to deep green, and on addition of sodium carbonate first to blue and then to red. This variety of tannin yields four anhydrides similar in character to those of the acid with 17 atoms of carbon.

Löwe (*Jour. Chem. Soc.*, xl. 901) gives $C_{28}H_{26}O_{15}$ as the formula of the hydrated tannic acid of oak-bark, and $C_{28}H_{22}O_{11}$ as that of the oak-red. Böttinger (*Ber.*, xvi. 2710) adduces evidence of weight in favour of $C_{19}H_{16}O_{10}$ as the formula of the tannic acid, and $C_{33}H_{26}O_{17}$ as that of the oak-red. He has also attributed to the latter the formula $(C_{14}H_{10}O_6)_2H_2O$ (*Jour. Chem. Soc.*, xxxviii. 650). To the tannin of oak-*wood* he attributes the formula $C_{15}H_{12}O_9$ (*Jour. Chem. Soc.*, lii. 584).[1]

Animal Tannin.

A body having the character of a tannin has been extracted from corn weevils (*Chem. News*, lvi. 175). Three per cent. was obtained of a substance forming small reddish-yellow scales soluble in water, alcohol, aqueous ether, &c., and precipitating gelatin, albumin, and alkaloids. It gave a bluish-black coloration with ferric salts, and on boiling with dilute sulphuric acid split up into glucose, gallic acid, and a red phlobaphene.

---

[1] It is probable that the discrepant statements respecting the composition of oak-bark tannin are due to the presence of two analogous bodies. According to F. Musset (*Jour. Soc. Chem. Ind.*, iii. 525) this is actually the case, both tannins being precipitable by gelatin and oxidisable by permanganate. One, which he terms oak-tannin, may be extracted by repeatedly agitating the infusion with acetic ether, in which the oak-red tannin is insoluble. He prefers, however, to determine the oak-red tannin by precipitation with iodine avoiding presence of air. The compound formed contains 7·8 per cent. of iodine and an equal quantity of iodine is converted into hydriodic acid. An equal quantity of the infusion is treated with zinc oxide, and, after twenty-four hours, and the absence of more than traces of tannin in the filtered solution being proved by gelatin and ferric acetate, the non-tannin matters are titrated with a decinormal solution of iodine. By deducting the amount of iodine, required by the non-tannin matters from that consumed by an equal measure of the original infusion, the iodine which has reacted with the tannins is found, and by subtracting from this twice the quantity of iodine contained in the precipitate of iodised oak-red tannin, the iodine corresponding to the oak tannin is ascertained. Examined in this manner, Musset found German oak-barks to contain from 7 to 8 per cent. of oak-tannin, and 6 to 10 per cent. of oak-red tannin.

Lupulotannic Acid. Hop-Tannin. $C_{24}H_{24}O_{13}$.

The tannin of hops is a glucoside which is easily soluble in water and proof spirit, but not in ether. It gives a green colour with ferric salts, a dirty green precipitate with cupric sulphate, a yellow with lead acetate, and a brownish-yellow precipitate with lime-water. It reduces Fehling's solution. Lupulotannic acid yields a precipitate with albumin but not with gelatin, unless it be previously dried at 100° C., by which treatment it is converted into the anhydride or phlobaphene, $C_{50}H_{46}O_{25}$, a body coexisting with lupulotannic acid in the hop, and having all the characteristics of a tannin. It precipitates gelatin solution completely, and reduces Fehling's solution. It is soluble in alcohol and in alkalies, and is precipitated on acidulating the latter solution.

Catechu-tannic Acid. Mimotannic Acid.

The tannins which yield catechol when heated differ from the pyrogallol derivatives by giving a green reaction with ferric acetate. Like oak-bark tannin, they give insoluble red phlobaphenes or anhydrides by the action of dilute acids. Their constitution is in most cases only very imperfectly understood, and even the composition of them is uncertain. The tannin of catechu is typical of this class of tannic acids.

Catechu-tannic acid, probably identical with the body described as mimotannic acid, is the astringent substance contained in catechu (cutch) and gambier.[1] It is extracted by cold water from catechu, and is also formed by heating catechin alone to 130°, with water to 110°, or by boiling it with alkalies. Catechu-tannic acid is a dark reddish-brown powder, moderately soluble in water, insoluble in ether, but readily soluble in alcohol and in acetic ether. It resembles gallotannic acid in many of its characters, but gives a greyish-green precipitate with ferric salts, and no reaction with ferrous salts. It is also distinguished from gallotannic acid by giving a dense precipitate with cupric sulphate and none with tartar-emetic; and by yielding catechol and phloroglucol by fusion with potash. The aqueous solution is precipitated by gelatin, albumin, and dilute sulphuric acid. When treated with hydrochloric acid and potassium chlorate in excess, catechu-tannic acid yields a chloro-substitution-product which is turned purple-red by sodium sulphite. Catechin gives the same reaction.

---

[1] It is doubtful whether the tannin of gambier is strictly identical with that of catechu.

Catechins.

Catechu and gambier contain from 20 to 30 per cent. of a body called catechin, which appears to be the type of a number of similar bodies occurring in all or most tannin materials yielding catechol-tannins. A catechin has certainly been recognised in Colorado quebracho, and the kinoïn of kino is a body of similar nature. The co-existence of several homologous or closely analogous bodies of the nature of catechin, even in catechu itself, is the probable explanation of the difference in the formula assigned to catechin by different observers. Unless qualified in some way, by the term catechin the body contained in catechu (cutch) or gambier is always understood.

CATECHIN may be prepared from gambier or catechu by digesting the powdered substance in cold water to remove the catechu-tannic acid, and exhausting the residue with boiling water. Impure catechin deposits as the solution cools, and may be redissolved in boiling water and decolorised by animal charcoal.

Catechin forms a white powder consisting of silky crystalline needles. It melts at 217° C. and yields a sublimate of catechol on further heating. It dissolves readily in alcohol and boiling water, but requires 1133 parts of cold water for solution. Agitation with ether or acetic ether extracts it from its aqueous solution, a fact which may be utilised for its purification. Though sometimes called catechuic acid, catechin possesses no acid properties, though it is soluble in alkalies. The alkaline solution turns brown on exposure to air. Catechin dissolves in strong sulphuric acid with deep purple coloration. The aqueous solution gives white precipitates with lead acetate and mercuric chloride, and reduces ammonio-nitrate of silver, but, unlike the tannins, does not precipitate gelatin, alkaloids, or tartar-emetic; on the other hand, it yields a precipitate with albumin. It is oxidised by permanganate in presence of free acid, a fact which may be utilised for its estimation (page 112). Heated under pressure to 140° with dilute sulphuric acid, catechin yields catechol and phloroglucol. With diazobenzene chloride, catechin gives a red crystalline precipitate, which is soluble in alcohol and ether, and dyes wool golden-brown.

Catechin is often described as an anhydride of mimotannic acid, the tannin of catechu and gambier, but according to Etti the opposite of this is probably the case. In constitution, catechin is probably a phloroglucide of tetra-hydrogenised protocatechuic acid. This view accounts for its decomposition by fusing caustic alkali with evolution of hydrogen and formation of protocatechuic acid and phloroglucol:—$C_6H_7.COOH : 2C_6H_3(OH)_2 + 4H(OH) = C_6H_3(OH)_2.COOH + 2C_6H_3(OH)_3 + 2H_2$.

Different observers, however, are not agreed as to the composition of catechin. Thus Liebermann and Tauchert, who prepared a crystallised diacetyl-derivative, attribute to catechin from catechu the formula $C_{21}H_{20}O_9 + 5H_2O$ (*Jour. Chem. Soc.*, xl. 53).

By the graduated action of heat or dilute acid on catechin it may be successively converted into the following anhydrides:—

Catechin, .	$2C_{19}H_{18}O_8 = C_{38}H_{36}O_{16}$	Not acid; does not precipitate gelatin.
Catechin-red; Catechu-tannic acid,	$C_{38}H_{34}O_{15}$	Acid; precipitates gelatin.
Di-anhydride, . .	$C_{38}H_{32}O_{14}$	
Tri-anhydride, . .	$C_{38}H_{30}O_{13}$	Insoluble in water.
Catechuretin,	$2C_{19}H_{14}O_6 = C_{38}H_{28}O_{12}$	

Kinoïn, $C_{14}H_{12}O_6$, a body resembling catechin, is obtained from green or Malabar kino by boiling with dilute hydrochloric acid, decanting from the precipitated kino-red, and agitating with ether. When recrystallised from hot water it forms small colourless prisms, which are difficultly soluble in cold water but readily in hot water and in alcohol. Its solution is coloured red by ferric chloride. Heated to 120°–130° it yields the anhydride, kino-red, $C_{28}H_{22}O_{11}$, and this when heated to 160°–170° gives $C_{28}H_{20}O_{10}$. Both anhydrides are precipitated by gelatin, but kinoïn itself is not. When heated with hydrochloric acid to 120°–130°, kinoïn yields methyl chloride, gallic acid, and catechol, and hence probably has the constitution of a guaiacol or methyl-catechol gallate.

Tannin-yielding Materials.

The following table gives the common names of the principal tannin-yielding substances used in commerce, together with the botanical names of the plants producing them, the parts of the plant used, and the usual percentage of tannin contained in good specimens of each material:—

Common Name of Material.	Botanical Name of Plant.	Part of Plant used.	Ordinary per cent. of Tannin.
Oak-bark, . .	Quercus pedunculata and Q. robur.	Bark.	8–13
Cork-bark, .	Quercus suber.	Inner bark.	10–14
Valonia, . .	Quercus ægilops.	Acorn-cups.	25–35
Chestnut-oak extract, .	Quercus (an American species).	Extract from bark.	20–25
Hemlock-bark, .	Abies Canadensis.	Bark.	10–14
,, extract,	Abies Canadensis.	Extract from bark.	18–28
Churco-bark, .	Oxalis gigantea (Chili).?	Bark.	26
Monesia-bark, .	Chrysophyllum glycyphlœum.	Bark.	32
Mangrove-bark,	Rhizophora mangla.	Bark.	9–33
Alder-bark, .	Alnus glutinosa.	Bark.	16
Larch-bark, .	Abies larix.	Bark.	6–8
Mimosa (Wattle),	Acacia dealbata and A. molissima.	Bark.	24–30

Common Name of Material.	Botanical Name of Plant.	Part of Plant used.	Ordinary per cent. of Tannin.
Catechu (Cutch),	Acacia and Areca catechu.	Extract from wood.	45–55
Gambier, . .	Uncaria gambir and U. acida.	Extract from leaves and small branches.	36–40
Sumach, . .	Rhus coriaria, R. cotinus, &c.	Leaves.	15–30
Chestnut-wood,	Castanea vera.	Wood.	8–10
,, extract,	Do.	Extract from wood.	14–20
Quebracho-wood,	Aspidospernum quebracho, &c.	Wood.	14–23
,, extract, solid,	Do.	Extract from wood.	53–60
,, ,, liquid,	Do.	Do. do.	36
Marsh Rosemary,	Statice coriaria.	Root.	20–24
Ratanhia,	Krameria triandria.	Root.	38–42
Myrabolanes, .	Terminalia chebula and T. belerica.	Fruit.	20–40
Divi-divi, . .	Cæsalpina coriaria.	Pod.	30–50
Kino, . .	Pterocarpus marsupium, and Drepanocarpus senegalensis.	Extract from fruit.	75
Gall-nuts, . .	Quercus infectoria, &c.	Galls.	60–77
Tamarisk galls,	Tamarix Indica, and T. Africana.	Galls.	50–54
Rove, . .	? (Greece and Asia Minor).	Galls.	24–34

C. Councler (*Jour. Chem. Soc.*, xlviii. 946) has published the following results.[1] The method of analysis is not stated,

	Moisture.	Tannin.	
		Total.	Readily Soluble.
Mimosa-bark, Tasmania, . . .	11·35	16·88	15·05
,, ,, . . .	8·25	23·12	19·93
,, Victoria, . . .	11·75	21·20	16·54
,, ,, . . .	9·25	17·30	12·70
Root-bark of Kermes Oak, "Garouille" (*Quercus coccifera*), . . .	10·00	8·69	7·88
Birch-bark, Friedrichsruh, . .	...	4·97	3·98
Alder-bark, Riesenthal, . . .	18·00	11·68	11·15
,, ,, . . .	10·70	7·38	5·35
,, ,, . . .	6·80	8·17	6·02
,, ,, . . .	10·50	12·53	11·82
,, ,, . . .	11·67	11·15	8·93
Willow-bark, Russian, *Salix purpurea*,	7·8	1·72	0·86
,, ,, *viminalis*	7·9	3·42	2·14
,, ,, *purpurea*,	8·7	4·71	2·70
,, ,, *capsica*,	13·4	2·62	1·34
,, ,, *amygdalina*,	7·6	3·17	2·27
Quebracho-wood (highest), . .	11·3	19·36	10·97
,, (lowest), . . .	10·0	16·42	7·66
Chestnut-wood, ...	7·3	8·49	5·48

---

[1] In the same paper Councler gives some interesting calculations of the price per kilogramme of the tannin present in various commercial extracts. Thus:—

Material.	Price per 100 kilos. in shillings.	Percentage of tannin.	Price of tannin per kilogramme (=2·19 lbs.) in pence.
Quebracho-wood, .	16–18	16–19	11
,, ,, extract,	16–18	36–60	14–18
Hungarian pine-bark,	11	12	12
,, ,, extract,	43	14	36
Oak-bark extract, .	55	...	38
Chestnut-wood, . .	8	8½	11
Sumach extract, .	92	8	54

but was probably von Schroeder's modification of Löwenthal's process.

The following results by Kay and Bastow (*Jour. Soc. Dyers and Col.*, iii. 132) were obtained by the assay of tanning materials exhibited in the Indian and Colonial Exhibition of 1886. The process employed was Procter's modification of Löwenthal's method (see page 110).

Tanning Material.	Percentage of Tannin.	
	In terms of Oxalic Acid.	In terms of Gallotannic Acid.
Terminalia tomentosa (galls), .	9·24	6·53
„ belerica (fruit), . .	12·86	8·48
„ chebula (fruit), . .	52·65	34·49
Ceriops Rosburghiana (bark), .	37·65	24·66
Camia auriculata, ...	19·94	12·86
Acacia catechu (extract), . .	76·00	...
„ „ (bark), . . .	21·35	...
„ arabica (pods), . . .	22·44	...
Areca catechu (nuts), . . .	14·28	...

Descriptions of a large number of tanning products (barks, leaves, kinos, &c.) of New South Wales have been published by J. H. Maiden (*Jour. Soc. Chem. Ind.*, vii. 38, 392).

The results of the assay of a large number of tannin matters by Procter's method are given on page 113.

F. Simand (*Jour. Soc. Chem. Ind.*, iii. 574) gives the following results of the assay of various tannin extracts by the Löwenthal-Neubauer method.

Extract from	Density, Beamé.	Tannin.		Remarks.
		Total.	Soluble in Cold Water.	
Quebracho-wood, solid,	...	73·08	70·09	Dried before analysis.
Valonia, solid, . .	...	70·44	68·59	Do.
Oak-wood, liquid, .	13°	14·47	15·09	Do.
Oak-bark, liquid, .	32°	24·37	23·72	Commercial extract.
Fir, liquid, . . .	32°	14·31	13·72	Do.
Chestnut-wood, liquid,	31°	23·52	22·68	Do.
Sumach, liquid, . .	34°	13·38	10·75	Do.

I. Ishikama has published the following figures showing the strength, in terms of gallotannic acid, of various tannin-yielding materials of Japanese origin (*Chem. News*, xlii. 274).

	Percentage of Tannin (in terms of Gallotannic Acid).
Gall-nuts (Japanese), ...	58·8 to 67·7
„ (Chinese), ...	77·4

	Percentage of Tannin (in terms of Gallotannic Acid).
Fruit of *Alnus firma*, ...	25·3 to 27·5
Bark of *Myrica rubra*, . , . .	10·5 to 15·0
Rind of Pomegranate, ...	20·4
Betel-nut, ...	18·0
Oak-bark (*Quercus dentata*) (inner), . .	7·4
,, ,, (outer), . .	2·6

QUALITATIVE RECOGNITION OF TANNING MATERIALS.

The table on next page, due to H. R. Procter, shows the behaviour of infusions of a number of commercial tannin matters with various reagents. The infusions must be very weak, not exceeding 1·002 in specific gravity, or precipitates may be formed where mere coloration or clouding is described as occurring. By means of the table, the origin of any simple tannin infusion is said to be ascertainable, but in the case of mixed infusions the indications are less reliable. In such cases, colour-reactions are apt to mislead, and it is safer to rely on the categorical test of precipitate or no precipitate, coloration or no coloration, without regard to the tint.

In some cases, only negative peculiarities are recorded, and the material cannot be positively identified in admixture with other tannin matters giving positive indications with the same reagents. Thus an infusion of myrabolanes could not be distinguished with certainty from an infusion of divi-divi, where any other material, such as gambier, was present, which gives a deep coloration with concentrated sulphuric acid.

In addition to the reactions described in the table, the identification of the products of the action of heat on tannins, and of their treatment with dilute acids and fusing caustic alkali, affords a valuable means of differentiation.

Most, if not all, of the ordinary varieties of tannin give with an ammoniacal solution of potassium ferricyanide a deep red coloraation, rapidly becoming brownish, especially on addition of excess of the reagent.

The extract from a bark yields more ash than that from a wood. The ash of an oak or pine extract contains manganese and has a green colour, or becomes green on being fused with sodium carbonate and a little nitre.

On shaking a concentrated solution of quebracho extract with acetic ether, the ethereal layer becomes at first green and then brown.

The bark and extract of the American chestnut oak (*Quercus castanea*) contains a substance exhibiting, like æsculin, a powerful blue fluorescence, especially in alkaline solution.

Reagent.	Myrabolanes.	Divi-divi.	Valonia.	Oak-Bark.	Chestnut Wood (Extract).
Boiled with equal volume of dil. sulphuric acid (1 to 9).	Pale deposit (ellagic acid) on cooling.	Pale deposit (ellagic acid) on cooling.	Slight pale deposit.	Slight pale deposit or turbidity on cooling.	Slight red deposit on cooling.
Bromine water.	No precipitate.	No precipitate.	No precipitate.	Pale precipitate.	No precipitate.
Dilute ferric chloride.	Blue-black precipitate.	Dark blue precipitate.	Blue-black precipitate.	Bluish-black precipitate.	Blue-black precipitate.
On adding ammonia.	Brown precipitate.	Dark red precipitate.	Red-brown precipitate.	Red-brown precipitate.	Dull red precipitate.
Sol. tartar emetic.	No precipitate.	Faint clouding.	No precipitate.	No precipitate.	Slight clouding.
Add ammonium chloride.	Light precipitate.	Dense precipitate.	Pale precipitate.	Whitish precipitate.	Pale precipitate.
Copper sulphate.	Faint clouding.	Slight green precipitate.	No precipitate.	Slight precipitate.	No precipitate.
On adding ammonia.	Dense dark precipitate.	Dense dark precipitate.	Dark reddish precipitate.	Brown precipitate.	Dark brown precipitate.
Lime-water.	Yellow precipitate turning greenish.	Yellow precipitate turning purple.	Yellow precipitate turning red-purple.	Brown precipitate.	Purplish-brown precipitate.
Ammonium molybdate in nitric acid.	Dirty yellow precipitate.	Dark greenish precipitate.	Dark greenish precipitate.	Greenish precipitate.	Dirty green precipitate.
With sodium sulphide exposed to air.	Yellow colour.	Yellow colour.	Turns purplish-red.	Turns red.	Reddish precipitate.
Add concentrated sulphuric acid to one drop of infusion.	Yellow colour.	Intense crimson.	Deep yellow.	Deep red precipitate on dilution.	Dark brown.
Lead nitrate.	Light yellow precipitate.	Dark yellow precipitate.	Pale precipitate.	Brown precipitate.	Brown precipitate.
Cobalt acetate.	Buff precipitate.	Buff pink precipitate.	Dirty pink precipitate.	Brown precipitate.	Dirty yellow precipitate.
Manganese acetate.	Yellow precipitate.	Yellow precipitate.	Dirty yellow precipitate.	Brown precipitate.	Grey precipitate.
Uranium acetate.	Dark red colour.	Dark red colour.	Dark red colour.	Dark brown precipitate.	Dark red colour.
Ammoniacal picric acid solution.	No precipitate.	No precipitate.	Brown precipitate.	No precipitate.	No precipitate.
Potassium bichromate.	Brown precipitate.	Brown precipitate.	Brown precipitate.	Brown precipitate.	Brown precipitate.

Hungarian Larch (Extract).	Hemlock (Extract).	Mimosa Bark.	Cutch (Pegu).	Gambier (Cube).	Gallotannic Acid, 1 per cent.
Yellow flocculent deposit separates quickly.	Abundant red floculent deposit.	Heavy red deposit on cooling.	Light red deposit on cooling.	Reddish deposit on cooling.	Usually some pale deposit.
Yellow precipitate.	Yellow precipitate.	Yellow precipitate.	Yellow precipitate.	Yellow precipitate.	No precipitate.
Dull brown precipitate.	Dirty green precipitate.	Full brown precipitate.	Green-black precipitate.	Intense green colour.	Blue-black precipitate.
Dull red precipitate.	Reddened precipitate.	Purple colour.	Dark red precipitate.	Reddened.	Reddened precipitate.
No precipitate.	No precipitate.	White precipitate.	No precipitate.	No precipitate.	No precipitate.
Pale precipitate.	Slight pale precipitate.	Dense white precipitate.	Pale precipitate.	Faint clouding.	White precipitate.
Slight cloud.	Pale precipitate.	Slight precipitate.	Dense precipitate.	No precipitate.	No precipitate.
Deep blue coloration.	Dark green coloration.	Deep red precipitate.	Deep violet coloration.	Dark green coloration.	Brown precipitate.
Dirty brown precipitate.	Brown precipitate.	Slight reddish precipitate.	Slight cloud, soluble in excess.	No precipitate.	Pale precipitate turning blue.
Slight clouding.	Slight precipitate.	Brown precipitate.	Slight cloud, soluble in excess.	No precipitate.	Yellow colour.
No change.	No change.	Turns red.	Slight reddening.	No change.	No change.
Dark brown or crimson.	Intense crimson.	Intense purple-red.	Deep red, no precipitate on dilution.	Dark brown or crimson.	Yellow.
Pale precipitate.	Pale precipitate.	Clouding.	No precipitate.	Faint clouding.	White precipitate.
Purplish precipitate.	Purple precipitate.	Brown precipitate.	Brown precipitate.	No precipitate.	Purple precipitate.
Slight clouding.	Slight precipitate.	No precipitate.	No precipitate.	No precipitate.	White precipitate.
Slight darkening.	Light brown precipitate.	Dark red colour.	Dark red colour.	Dark red colour.	Crimson colour. Brown precipitate.
No precipitate.	Clouding.	No precipitate.	No precipitate.	No precipitate.	No precipicipitate.
No precipitate.	Brown precipitate slowly formed.	Brown precipitate.	Brown colour.	Brown precipitate slowly formed.	Brown precipitate.

Sumach extracts are distinguished by a peculiar tarry smell, and yield a high ash.

The following are detailed descriptions of certain tannin matters. The methods of assaying them for their content of tannin will be described in the sequel.

CATECHU or CUTCH is the dried extract from the wood of the *Acacia catechu* and allied species. It is very similar in nature to gambier. Cutch, however, produces a hard red leather-like *Mimosa*, and generally occurs in more or less brittle, splintery masses. Gambier occurs in light, porous brown cubes, more or less adherent, or in blocks measuring 2 feet × 1 foot × 9 inches, soft internally and wrapped in matting. *Terra japonica* is a trade-name, now somewhat obsolete, for both cutch and gambier.

In addition to a large proportion of a variety of tannin (catechu-tannic acid), catechu contains 30 or 40 per cent. of catechin (page 79), which is deposited on cooling a boiling aqueous solution.

Catechu is not unfrequently adulterated, starch, sand, clay, and blood being among the materials employed for the purpose, and Jessart states he has met with an admixture of 60 to 70 per cent. of ferrous carbonate. Catechu should not yield more than 5 per cent. of *ash*. *Starch* may be detected by treating the sample with alcohol, boiling the insoluble residue with water, and testing the cold liquid with iodine, which gives the well-known blue colour in presence of starchy matters. The presence of *ordinary tannin-matters* is indicated by the modified colour which the sample gives with ferric salts, pure catechu giving a decided green. *Blood* may be detected by treating the sample with alcohol, and drying and heating the residue in a tube, when ammonia and most offensive vapours will be produced. Aqueous solution of catechu should give with albumin or gelatin an abundant precipitate; with salts of tin and lead, yellow precipitates of various tints; and a brown precipitate with bichromate of potassium. It should take a decided brown hue with alkalies, and give a greenish colour with ferric chloride. Good catechu yields at least half of its weight to ether and should be entirely soluble in boiling water, the latter solution depositing catechin on cooling. Catechu does not wholly dissolve in cold water unless it has been previously modified by age or exposure to damp.

An aqueous solution of *Pegu* cutch gives dense precipitates with bromine-water and cupric sulphate, neither of which reagents affects gallic, gallotannic, or pyrogallic acid. In dilute solution, Pegu cutch does not precipitate potassium bichromate, but gallotannic acid does.

The proportion of tannic acid in catechu is best determined by Löwenthal's gelatin-permanganate process (page 110). The proportion of catechin may be roughly deduced from the volume of permanganate decolorised after removal of the mimotannic acid by means of gelatin. More accurate results are obtainable by employing a moderate excess of gelatin, removing the catechin from the filtrate by agitation with ether, evaporating the ethereal liquid, dissolving the residue in warm water and titrating with permanganate.

Kino generally occurs in irregular black fragments, but it is also met with in round cakes. Thin slices are often transparent and of a reddish colour; the powder is red. Kino should be completely soluble in hot water, forming a red liquid which gradually becomes turbid. Kino is sometimes adulterated, the usual sophistications being dragon's blood, pitch, catechu, and ratanhia extract. The last substance may be distinguished from kino by touching a fragment of the sample with the tongue; kino remains reddish-brown, but ratanhia extract takes a fine bronze tint, which lasts as long as the surface of the fragment is wet. The ash of kino should not exceed 3 or 4 per cent.

Divi-divi is composed of the bean-like pods of *Cæsalpina coriaria*, a small tree found in the neighbourhood of Maracaibo and other parts of South America. The pods are about three inches long, brown or blackish in colour, and generally folded up or bent into the shape of a letter S. The best pods are thick and fleshy, and of a comparatively pale colour. Deep brown pods with black patches have been gathered when wet, or subsequently exposed to damp, which injures them considerably.

Galls is a generic name applied to those excrescences on plants produced by the punctures of insects for the purpose of depositing their eggs. Galls are the most valuable and important of all tannin matters.[1] *Nut-galls, oak-galls, Aleppo or Turkey-galls* are the produce of the female of an insect called *cynips* (gall-wasp), which pierces the buds on the young branches of the *Quercus infectoria* and other species of oak. The eggs therein deposited soon hatch, while the bud loses its natural growth and swells out to the size of a hazel-nut. When perfect, the insect punctures a hole and escapes. Good gall-nuts should not be so pierced; they should be heavy, and of a fresh green or blue colour ("green galls"). If the insect has escaped, they are yellow and inferior ("white galls").

---

[1] A sample of gall-nuts analysed by Guibourt contained:—tannic acid, 65·0; gallic acid, 2·0; ellagic and luteo-gallic acid, 2·0; chlorophyll and volatile oil, 0·7; brown extractive matter, 2·5; gum, 2·5; starch, 2·0; woody fibre, 10·5; sugar, albumin, and ash, 1·3; water, 11·5 per cent.

The best oak-galls contain 60 to 70 per cent. of gallotannic acid, and about 3 per cent. of gallic acid.

Worm-eaten galls are sometimes doctored by filling the holes with wax. The fraud may be detected by immersing the galls in boiling water, which melts the wax and renders the holes visible. Exhausted galls are occasionally coloured by washing them with a solution of ferrous sulphate, which is readily detected by its chemical reactions.

Knoppern are galls formed from immature acorns of several species of oak, and are largely used for *tanning* throughout Austria. In a large number of samples of Austrian galls of the year 1884, Eitner found from 28 to 35 per cent. of tannin, the moisture being about 12 per cent. (*Jour. Chem. Soc.*, xlviii. 947).

Chinese and *Japanese gall-nuts* are a production of the *Rhus semialata.* They are very light and hollow, and distorted by numerous protuberances, and are completely covered by a thick velvety grey down. Chinese galls are much used for the preparation of tannin, of which they contain about 70 per cent. English galls from the common oak are much inferior to the foreign varieties. They are smooth, brown, and slightly speckled with pale brown excrescences. The Japanese are smaller, paler, and generally more esteemed.

MYRABOLANES are the fruit of several species of *Terminalia.* In size and shape the myrabolane resembles a slightly shrivelled plum. As imported, myrabolanes contain from 3 to 7 per cent. of moisture, and have about 10 per cent. of ash on ignition. The tannin is chiefly contained in the dried pulp enclosing the stone.

Good myrabolanes should be of a pale buff colour, plump, or but slightly shrivelled, and free from worm-holes or blackish stains or blotches. They should be hard and firm, and when broken with a hammer should form a light-coloured dry powder and irregular fragments. If they crumble between the fingers to a dark coloured dust, or flatten under the hammer, they are inferior. The stones contain very little tannin, and hence their proportion should be ascertained by breaking 50 nuts with a hammer, clearing the stones from any adherent pulp, and weighing them separately. They may constitute from 23 to 52 per cent. of the whole fruit.

Ground myrabolanes should be light in colour, dry, and free from a saline or an intensely bitter taste. When slightly moistened and rubbed in the hand they should adhere very tenaciously to the skin.

Myrabolanes are sometimes mixed with earth, sand, *nux vomica*, betel-nuts, and a variety of seeds and berries. They may also be adulterated with finely-ground divi-divi, wild galls, and old and worthless sumach. On scattering the powdered substance on a sheet of paper, and examining it with a lens, it will be recognised by the fragments of its brown, flat, smooth pea-like seeds, which from their hardness and smoothness, escape being crushed to powder. The leaf stalks of sumach are readily distinguished from the torn, irregular fibre of the myrabolanes.

Sumach, or Shumac, consists of the leaves, leaf-stalks, and small twigs of several species of *Rhus*. It is sometimes sold whole, sometimes coarsely bruised, but more commonly in fine powder. The best Sicilian sumach gives a bright green powder which has a pleasant tea-like odour. The second quality is reddish-yellow; and Spanish sumach has usually a fawn-colour.

Sumach should be quite dry, and free from cakes or lumps, the presence of which shows the sample has been exposed to damp and will probably have become seriously deteriorated. The colour should be bright. If dull, the sample is probably damaged by long keeping, or is mixed with sumach of inferior quality.

Sumach sometimes contains a notable proportion of earth or sand; 10 per cent. of ash is sometimes left on ignition.

Valonia consists of the acorn-cups of certain species of oak, chiefly exported from Smyrna, but also obtained from other parts of Asia Minor, as well as from Greece and the Grecian Archipelago. They should be of a bright drab colour. If dark they have suffered from damp, and will be deteriorated in quality.

Determination of Tannin. Assay of Tanning Materials.

A great number of methods have been descibed for determining tannin and assaying tannin-yielding materials.[1] In many instances the authors have ignored the fact that gallic acid, while reacting in many respects like tannin, does not form stable insoluble compounds with gelatin and albumin, and hence is valueless for the purpose of tanning.[2]

---

[1] The methods of assaying tannin-yielding materials have been ably examined by H. R. Procter, and it is largely from his published descriptions that the matter in the test is derived. It may be added that the whole article on tannins, substantially in its present wording and shape, has been in manuscript since the early part of 1884, when Mr Procter kindly undertook its perusal and correction, and with the author's consent incorporated some portions of it in his valuable *Text-Book of Tanning* (E. & F. N. Spon., 1885). The proof-sheets have also been recently submitted to Mr Procter.

[2] A little consideration of the subject will show that a general method of determining the tannin in all kinds of tanning matters is not likely to be devised. The problem is comparable to that of devising a general and simple method of determining the metals forming coloured salts,—say copper, iron, chromium, cobalt, and nickel,—in presence of zinc, aluminium, and lead, the

SAMPLING OF TANNING MATERIALS is often a troublesome operation, and together with the difficulty attending complete extraction is a fertile source of error.

When available, a steel-mill is the best means of roughly pulverising most tanning materials. With the exception of barks, the grinding can be effected by a disintegrator with fine screens, taking great care to prevent the escape of dust. Barks may be sampled by cutting each fragment with a small circular saw or rasp driven by a lathe, and collecting the dust.

In the absence of the foregoing appliances, bark and valonia may be cut with strong shears, and myrabolanes broken roughly with a hammer. In sampling valonia care must be taken to get a due proportion of the beard, and in taking myrabolanes it must be remembered that the bad berries are light and work towards the top of the bag. The sample being partially reduced by one of the above means, the moisture (usually 15 to 16 per cent.) must be determined by drying at 100° C., and the thoroughly dried sample further ground by passing it through a coffee-mill. The ground sample must be again dried before weighing for analysis, as it is very hygroscopic.

THE EXTRACTION OF TANNIN-MATTERS is better effected by treating the sample at once with a large quantity of water than by repeated treatment with smaller quantities. 10 grammes weight of valonia or myrabolanes, 20 of oak-bark, or a corresponding weight of other tanning material is placed in a flask of at least 1½ litres capacity and covered with 1 litre of cold distilled water. This is raised to ebullition (great care being necessary at the moment of boiling to prevent frothing up and boiling over), and the liquid is kept boiling briskly for half an hour, a funnel being placed in the mouth of the flask. The liquid is then allowed to cool, rinsed with the solid residue into a litre flask, which is filled with cold water to the mark, and the solution well shaken and filtered. If the solution is obstinately turbid it may be clarified by agitation with kaolin, followed by re-filtration. With tannin-matters which are apt to deposit ellagic acid or red anhydrides (phobaphenes), higher results are obtained if the solution is cooled rapidly and filtered at once than if it is allowed to stand for twenty-four hours. Hence, in this respect, a uniform practice is desirable. If the

salts of which are usually colourless. It is easy to separate copper from zinc, iron from aluminium, and nickel from lead, but there is no method which will separate copper, iron, and nickel at one operation from zinc, aluminium, and lead. If, in addition, it were extremely difficult to obtain some of these metals in a state of purity, and they were liable to change by the action of reagents, the problem would be rendered still more difficult. Yet this fairly represents the position of the chemistry of the tannins.

titration is not to be performed at once, 0·5 c.c. of glacial acetic acid should be added to check oxidation. In dissolving *extracts*, it is desirable to pour them into water actually boiling, as many become permanently insoluble if first mixed with water at too low a temperature.

Of the numerous methods which have been devised for the assay of tannin-matters, nearly all those worthy of detailed description are based on the principle of precipitation of the tannin by a solution of gelatin or its absorption by a gelatinous substance. In some cases the weight of the precipitate formed, or the increase in the weight of the solid gelatinous substance has been ascertained, but a preferable plan is to ascertain the quantity of tannin precipitate by comparing the liquid after the treatment with the original untreated solution. This is done by Hammer by taking the specific gravity; by Simand and Weiss by weighing the solid matter left on evaporation; and by Löwenthal by determining the volume of standard permanganate solution decolorised by the solution before and after removal of the tannin. These methods, which appear simple enough in principle, are in practice surrounded with very considerable difficulties, especially when considerable quantities of gallic acid are present.

THE OXIDATION-METHOD OF TANNIN ASSAY.

This process, which was first worked out by Löwenthal, is based on the fact that tannin is oxidised in acid solutions by permanganate, though the slowness of the oxidation and the want of definition of the end-reaction render the method unsuitable without modification. By addition of a considerable quantity of indigo the oxidation of the tannin is controlled, and the end-reaction is rendered perfectly definite. As solutions of commercial tannin-matters contain other oxidisable matters besides tannins, it is necessary to separate these and titrate a second time, in order to ascertain the volume of permanganate actually required by the tannin present. This separation may be effected by digestion with hide-raspings, or more conveniently by a solution of gelatin, the use of which was first suggested by Estcourt.

In practice, Löwenthal employs a mixed solution of gelatin and common salt, to which a small quantity of sulphuric or hydrochloric acid is added. In using this form of the process it is generally necessary to let the mixture stand several hours in order to obtain a clear filtrate, besides which the gelatin remaining in solution (or its associated impurity) has a slight though generally negligible reducing action on the permanganate. In some cases, even after long standing, filtration is very tedious, and it has also been proved by F. Simand (*Jour. Chem. Soc.*, xlii. 1237), that a certain proportion of the tanno-gelatin precipitate, varying with the acid and kind of tannin present, remains in solution, and hence that the results obtained by the process are below the truth.

On account of the objections to Löwenthal's process as commonly conducted, H. R. Procter has recently proposed a modification of it (*Jour. Soc. Chem. Ind.*, iii. 82), in which the excess of gelatin is removed by saturating the liquid with common salt, and the filtration is facilitated by addition of kaolin. A perfectly clear filtrate wholly free from tannin, and nearly so from gelatin, is thus obtained without difficulty. The following are the details of the process:—

a. 10 grammes of a sample of sumach or valonia, or 20 grammes of finely-ground bark, are exhausted by boiling with water in the manner described on page 108, and the infusion allowed to cool and diluted to 1 litre. 5 c.c. measure of this solution is run into a porcelain basin and diluted to 750 c.c. by addition of distilled or good drinking water, and 20 c.c. added of an indigo solution, a litre of which contains 5 grammes of the purest indigo-carmine,[1] and 50 c.c. of concentrated sulphuric acid. A solution containing 1 gramme of potassium permanganate per litre is then dropped in very slowly with vigorous stirring, until the liquid becomes transparent, when the addition is continued more cautiously, with occasional pauses, until the clear yellow liquid appears of a faint pink colour on the margin. The titration is repeated, the measures of permanganate required in the two cases being added together and called *a.*

In employing the oxidation-process, it is essential that the volume of permanganate required by the tannin should *in no case* exceed two-thirds of that reduced by the indigo. If the result of the titration shows that this proportion has been exceeded, the experiments must be repeated with a smaller quantity of the tannin solution.

b. 50 c.c. of the tannin solution should be mixed in a flask with 28·6 c.c. of a freshly made and filtered solution of gelatin[2] (2 grm.

---

[1] The indigo-carmine (sodium sulphindigotate) must be of such quality that the solution when oxidised by permanganate is a pure yellow colour, from a trace of brown or orange. Any contamination with indigo-purple, which gives brown oxidation-products, is quite fatal to the accuracy of the analysis. A suitable material for the purpose may be obtained from Mawson & Swan, of Newcastle-on-Tyne. The indigo solution should be of such strength that 20 c.c., diluted to 750 c.c. with water, shall require from 14 to 16 c.c. of standard permanganate for its oxidation.

[2] 2 grammes weight of Nelson's or other good gelatin is allowed to swell in distilled water for a few hours, then melted by immersing the flask in boiling water, and the resultant solution made up to 100 c.c.

per 100 c.c.). After shaking, the liquid is saturated with common salt,[1] which increases the volume to 90 c.c. 10 c.c. of dilute sulphuric acid (containing 1 volume of the concentrated acid in 10) should next be added, and then about 10 grammes of pure kaolin or barium sulphate. The flask should now be vigorously shaken for a few minutes, and the liquid passed through a dry filter. This is effected rapidly, and the filtrate is perfectly clear. Two quantities of the filtrate of 10 c.c. each ($=5$ c.c. of original infusion) are then treated with indigo solution, and titrated with standard permanganate as before, the result being called b. The difference $(a-b)$ between the measure of permanganate employed for the two quantities of unprecipitated tannin infusion (a), and that decolorised by the two portions of the filtrate, gives the volume of permanganate solution decolorised by the tannin in 10 c.c. of the original infusion.

c. 10 c.c. of a decinormal solution of oxalic acid (6·3 grammes of crystallised oxalic acid, $C_2H_2O_4+2H_2O$, per litre) is diluted with distilled water to about 500 c.c., warmed to about 60° C., 20 c.c. of pure dilute sulphuric acid added, and standard permanganate run in with constant stirring till a pink coloration, remaining permanent for a minute, shows that oxidation is complete. The volume of permanganate consumed, which is called c, is evidently that required for the oxidation of 63 milligrammes of crystallised oxalic acid.

The proportion $c:(a-b)=63:x$ will give the number of milligrammes of oxalic acid corresponding in reducing power to the tannin in 10 c.c. of the infusion assayed. If 10 grammes of the sample were extracted and the solution made up to 1 litre, 10 c.c. of the infusion represented 0·1 gramme of the tanning material, and hence the number of milligrammes of oxalic acid will be *the percentage of tannin expressed in terms of crystallised oxalic acid.* It is frequently convenient to express the results of the assay in this way, since what is required in practice is not the absolute weight of tannin in the various materials, but their *comparative* richness in tannin. It would of course be of interest to express the results of tannin-assays in actual percentages of tannin, but unfortunately the different varieties of tannic acid have different reducing powers, and the expression of the results of the assay of oak-bark or cutch in terms of gallotannic acid would be more objectionable than the expression of assays of all kinds of tannin-matters in terms of oxalic acid.[1] The actual reduction-equivalents of the different kinds of tannin are very imperfectly known. Neubauer states that of gall-tannin at 41·57; that is, 41·57 grammes of gall-tannin possess the same reducing power on permanganate that is possessed by 63 grammes of crystallised oxalic acid ($C_2H_2O_4,2H_2O$), or 56 grammes of iron in the ferrous state. This is tantamount to the statement that 41·57 grammes of gall-tannin decolorise a volume of permanganate solution yielding 8 grammes of available oxygen. Neubauer's equivalent for gallotannic acid has been confirmed by Ishikawa (*Chem. News*, xlii. 274), who found 41·688 as the figure for the tannin of *Kibushi*, or Japanese gall-nuts. Councler and von Schroeder, on the other hand, find the equivalent to be only 34·25.[2] For oak-bark tannin, Neubauer gives the equivalent 62·36, which is confirmed by Oser's figure, 62·35, and approximately by that of Simand, 61·1. The reduction-equivalents of other varieties of tannin are almost wholly unknown.[3] Oser's and Neubauer's figures for oak-bark tannin show a reducing power nearly identical with that of oxalic acid (=63), and hence, in the present state of the subject, the results of the titration may be conveniently expressed in terms of oxalic acid. An alternative plan is to state the strength of the tannin-matter in terms of "oxygen consumed." Each 1 c.c. of a solution of potassium permanganate (containing 1 gramme of the salt per litre) which may have been decolorised by the tannin, represents 0·000253 of "oxygen consumed," or 0·00199 (practically 0·002) gramme of crystallised oxalic acid. Neubauer's equivalent for gall-tannin is practically two-thirds of the bark and oxalic acid figures. The first figure is applicable to galls, and probably to divi-divi, sumach and myrabolanes; the second to oak-barks, and probably to oak-wood, valonia, chestnut extract, &c. Gallic acid consumes a greater volume of permanganate than the tannin from which it is derived. Hence, as commercial tannin is often largely contaminated with gallic acid, it not unfrequently shows over 100 per cent. of tannin when assayed.

---

[1] B. Hunt (*Jour. Soc. Chem. Ind.*, iv. 263) has shown that the excessive quantity of salt recommended by Procter causes the precipitation of a notable quantity of gallic acid when much is present. Hence, he prefers to mix 50 c.c. of the tannin solution with 25 c.c. of a 2 per cent. solution of gelatin, and then add 25 c.c. of a saturated solution of common salt containing 50 c.c. of strong sulphuric acid per litre. Kaolin is next added, and the mixture well agitated and filtered, and in all other respects Procter's method of operating is adhered to. Hunt's modification is approximately a return to Löwenthal's original method, and introduces its attendant error. Hence Hunt's mode of working is only to be recommended in presence of much gallic acid.

---

[1] Von Schroeder has suggested the use as a standard of commercial gallotannic acid, the moisture in which has been determined by drying at 95° C., and which has been proved to contain not more than 5 per cent. of non-tannin matters unprecipitable by hide or gelatin; dividing the result obtained by 1·05 to allow for the slightly higher reducing power of the impure tannin. Procter has proposed to employ gallic acid for standardising the permanganate, as it is readily obtained pure, and is oxidised in presence of indigo in a manner very similar to gallotannic acid.

[2] This discrepancy has been shown by von Schroeder to be due to the different manner in which the permanganate was added in the titration, Neubauer employing the "drop method," while Councler and von Schroeder added the solution in successive quantities of 1 c.c. with a short interval between each addition. This modification seriously effects the volume of the standard solution consumed (see page 116).

[3] The figures recorded by Günther are so remarkably at variance with those of the observers quoted in the text, that there is probably some undiscovered error. His results were :—gallotannic acid, 16·25; sumach tannin, 16·5; caffetannic acid, 17·0; oak-bark tannin, 16·0; kinotannic acid, 14·0; ratanhia-tannin, 17 to 18·5; and tormentilla-tannin, 17·5. He also gave some figures for mimotannic acid and catechin, which when corrected for an error of calculation are 2·77 and 2·66 respectively. Lehmann, in checking these ex-

According to Cech (*Zeitschr. Anal. Chem.*, vii. 134), no interference in the estimation of tannin by permanganate is produced by the presence of acetic acid, citric acid, tartaric acid, malic acid, cane-sugar, dextrin, gum, fat, caffein, or urea, provided the solution be properly diluted.

It cannot be too clearly understood that the permanganate and all other processes for the assay of tannin-matters are merely comparative, and give results worthy of acceptance only when they are used for comparing the qualities of samples of material of the same character. Thus, bark may be compared with bark, valonia with valonia, and cutch with cutch, but *all cross comparisons are misleading;* and would be so even if the exact percentage of tannin could be calculated, since the practical and commercial value of tanning materials does not depend on the quantity of tannin only, but on the colour and quality of the leather, though the same process should give absolute results of at least approximate accuracy when applied to different materials containing the same variety of tannin.

The following figures by Procter show the results to be expected when applying the permanganate process to the assay of various tannin-matters. The determinations were made by the method already described.

---

periments, found the equivalent 2·57 for mimotannic acid and 2·42 for catechin. There is evidently something grossly wrong here, for it would result in a sample of cutch which showed 63 per cent. of tannin expressed in terms of oxalic acid being stated to contain only 2·67 per cent. of catechu-tannic acid, though a far larger proportion than that could be actually prepared from it.

	In terms of Oxalic Acid.	
	Tannin.	Other oxidisable bodies.
Valonia; good Smyrna, ...	29·1 per cent.	2·3 per cent.
,, ,, ...	30·7 ,,	2·1 ,,
,, ,, ...	30·5 ,,	1·9 ,,
,, ,, ...	32·6 ,,	2·7 ,,
Hungarian larch extract, . . .	14·78 ,,	1·95 ,,
,, ,, ,, ...	18·08 ,,	2·33 ,,
Chestnut-wood extract (sp. gr. 1·205),	25·53 ,,	3·68 ,,
Pegu cutch, ...	63·59 ,,	2·45 ,,
Spent liquor,[1]	0·12 ,,	11·0 ,,

The permanganate process has been applied by A. Hill to the determination of tannin in *tea* (*Analyst*, vi. 95). The average proportion of tannin, in terms of oxalic acid, found in the thirty-two samples of tea examined was 14·8 per cent., the extreme results being 6·18 in black Assam tea and 26·90 in a black caper tea. Other determinations of the proportion of tannin in tea have been made by O. Kellner (*Jour. Chem. Soc.*, lii. 73) and J. F. Geisler (*Analyst*, ix. 220).

The following figures are due to B. Hunt (*Jour. Soc. Chem. Ind.*, iv. 264). They show the insoluble matter and total extract of various commercial tanning materials, together with the oxalic acid equivalents of the total oxidisable matters, and of the tannin as precipitated by Procter's and Hunt's methods.[2] The difference between the results obtained by these two methods is attributed by Hunt to the precipitation of gallic acid by the saturated brine employed by Procter.

---

[1] The results of the assay of the spent liquor are instructive. The liquor originally contained from 10 to 15 per cent. of the tannins from oak-bark, valonia, myrabolanes, gambier, hemlock, &c., which contact with hide had reduced to the small proportion of 0·12 per cent. That a portion had not been absorbed but decomposed is shown by the large accumulation of oxidisable impurities (equal to 11 per cent. of oxalic acid). Spent liquors are very pale in colour, as also are the filtrates from the gelatin precipitation, a fact that proves that the colouring matters present in tanning materials resemble tannin in their behaviour to hide and gelatin.

For the method of examining *tan-liquors*, see page 125.

[2] Hunt states in the same paper that treatment with gelatin and salt does not remove all that is of tanning value from solutions of gambier and allied materials, and hence he recommends the removal of the tannin in such cases by means of purified skin-shavings. These he adds in the proportion of 5 grammes to 100 c.c. of a 1 per cent. gambier solution, and after twelve hours

Material.	Insoluble Matter.	Total Extract.	In terms of Oxalic Acid.		
			Total oxidisable Matters.	Tannin, Procter.	Tannin, Hunt.
"Pure tannin,"	...	...	135·76	122·44	121·98
English oak-bark,	66·15	18·38	15·70	13·54	11·97
Canadian hemlock-bark,	75·25	13·96	9·03	7·46	7·08
Larch-bark,	60·80	20·64	8·20	7·17	6·15
Mangrove-bark,	49·70	26·60	31·35	29·71	28·48
Alder-bask,	68·00	19·36	8·27	6·15	5·73
Valonia,	46·05	38·50	37·41	35·24	30·50
Myrabolapes,	...	42·80	48·23	38·43	38·00
Sumach,	47·77	44·10	42·53	34·30	31·46
Turkish blue galls,	36·35	48·40	73·38	65·83	59·96
Aleppo galls,	14·32	68·80	98·85	87·82	83·05
Wild galls,	54·17	81·70	26·21	18·75	16·56
Divi-divi,	29·90	54·38	66·68	62·62	61·22
Pomegranate rind,	49·50	41·00	27·58	24·18	23·12
Tormentil root,	67·95	19·70	22·27	20·98	20·68
Ratanhy root,	66·00	18·80	22·27	20·15	19·30
Pure Indian tea,	53·40	34·46	23·06	18·65	17·40
Pure China tea,	62·60	24·50	18·03	14·21	14·09
Cutch,	4·75	61·60	57·65	51·95	44·24
Gum kino,	1·00	79·80	66·39	59·55	51·55
Hemlock extract,	...	48·78	35·16	33·17	30·98
Oak-wood extract,	...	37·78	33·49	26·90	23·86
Chestnut extract,	...	50·28	39·77	32·63	28·88
Quebracho extract,	...	49·00	48·22	44·45	40·84
Tan-liquor (sp. gr. 1·030),	...	6·01	4·84	3·14	2·10
Spent liquor (sp. gr. 1·0165),	...	3·10	1·40	0·37	0·25

A few years since, the permanganate process of determining tannin was submitted to a careful examination by a commission of German chemists. After reviewing earlier methods, they recommended the following modifications of the permanganate process for general adoption:—1. That the *permanganate* solution contain 10 grammes of $KMnO_4$ in 6000 c.c. 2. That the *indigo-solution* should be made by dissolving 30 grammes of air-dry sodium sulphindigotate in 3000 c.c. of dilute sulphuric acid (1 : 3), 3000 c.c. of water added, the whole shaken till dissolved, and the liquid

filters and titrates the filtrate with permanganate in the usual way. The following results were obtained :—

	Insoluble Matter.	Total Extract.	In terms of Oxalic Acid.	
			Total oxidisable Matter.	Absorbed by Skin.
Cube gambier,	5·31	74·40	70·12	51·07
Sarawak „	3·67	70·70	63·13	47·09
Bale „	1·40	63·54	56·00	43·70

filtered. 20 c.c. of this solution in 750 c.c. of water should be used in each titration, and should reduce about 10·7 c.c. of the permanganate solution. 3. *Hide powder* is substituted for the ordinary gelatin solution. It must be white, and in a fine woolly state of division, and should yield to cold water no substance capable of reducing permanganate.[1]

Instead of adding the permanganate solution drop by drop, the commission recommend (with very doubtful advantage) that an addition be made of 1 c.c. at a time, and the mixture vigorously stirred for five or ten seconds after each addition. As soon as the liquid has become bright green, two or three drops at a time should be cautiously added with stirring, till the liquid is pure yellow. The results obtained by the "1 c.c. method" differ considerably from those obtained by the ordinary or "drop method," which was that employed by Neubauer and Oser for the determination of the reduction-coefficients of tannins. It has, however, been shown by H. R. Procter (*Jour. Soc. Chem. Ind.*, v. 79), that the results are more influenced by the rapidity of mixing than by actual time, and that the 1 c.c. method, while it always gives a higher consumption of permanganate than the drop method, is even more affected by variations in stirring.[2]

To determine the oxidisable matters "not tannin," 50 c.c. of the infusion should be digested in the cold with 3 grammes of the hide powder (previously moistened with water, and well squeezed in linen). The liquid is frequently agitated during eighteen to twenty-four hours, and is then filtered, and 10 c.c. titrated in the usual way.

F. Simand has recommended the use of the purified gelatinous matter of bones as acting more quickly than hide powder (*Jour. Soc. Chem. Ind.*, i. 509). Tubular bones, freed from joints and marrow, are crushed and soaked for two days in a 5 per cent. solution of soda, then thoroughly washed with water, reduced to smaller pieces, and treated with dilute hydrochloric acid until softened. They are then again washed, and passed through a small grinding machine while still wet. The comminuted mass is treated with very dilute hydrochloric acid, thoroughly washed, pressed and dried.

---

[1] Hide powder of suitable quality is prepared by Dr Roth of Berlin, and is obtainable from Messrs Mawson and Swan, of Newcastle-on-Tyne.

[2] Procter points out that the limit of the reaction is not a complete oxidation of the organic matter, but only a partial one of the bodies more readily oxidisable than indigo; and hence towards the end of the operation, when the indigo has become scarce, the permanganate is partially consumed in further oxidising the products of the normal reaction; and that this is least the case when the permanganate is added slowly and rapidly mixed with the liquid, so as to bring it into immediate contact with the remaining indigo. Procter obtained very uniform results by the use of a stirrer consisting of a perforated porcelain disc, which was worked up and down in the beaker by means of attached glass rod; and the results were still further improved by attaching a capillary jet to the point of the burette, and allowing the permanganate to run in steadily throughout the titration.

E. B. (*Jour. Chem. Soc. Ind.*, vi. 51) suggests the use of ferric acetate instead of gelatin for precipitating tannin. The process has only been tried on gall-tannin, and F. Gantler (*Jour. Chem. Soc.*, liv.) doubts its accuracy in this case.

Other operators have recommended the use of an ammoniacal solution of copper for removing the tannin. This modification is not capable of general application. *Sumach*, however, is a tanning material which may be advantageously precipitated by ammonio-cupric acetate, with titration of the solution by permanganate and indigo before and after the treatment.[1]

N. H. Darton (*Jour. Amer. Chem. Soc.*, May 1882) employs ammonio-sulphate of copper in the following manner:—Twenty grammes weight of *hemlock-bark*, or an equivalent amount of other tanning material, is extracted first with cold and then with several quantities of boiling water. The mixed infusions are treated with 25 c.c. of dilute sulphuric acid (1 : 10), the liquid filtered, and the filtrate rendered slightly alkaline with ammonia, any precipitate being filtered off. A further quantity of 25 c.c. of dilute sulphuric acid is then added, and the liquid made up to 1 litre. 100 c.c. of this solution is treated with an equal measure of a solution of cupric sulphate (containing 1¼ per cent. of the salt), to which sufficient ammonia has been added to dissolve the precipitate first formed. The liquid is passed through a dry filter, and a definite measure of the filtrate neutralised and titrated for "not tannin" with indigo and permanganate in the usual way. H. R. Procter states that the preliminary treatment with acid and ammonia is unnecessary in the case of *valonia* (and probably in that of oak-bark), and that the process gives results practically identical with the improved gelatin method, while it is much less troublesome. With *chestnut extract* the results are satisfactory, provided the preliminary treatment be omitted, as this removes 75 per cent. of the matter precipitable by gelatin, and cutch behaves similarly. On the other hand, a sample of *larch extract* which tanned well, and showed 18 per cent. of tannin by the gelatin method, gave *no* precipitate with the ammonio-cupric solution. This peculiarity would allow of the estimation of valonia-tannin in presence of larch-tannin, and the same principle might be utilised in other cases.

---

[1] By this process, I. Macagno (*Chem. News*, xli. 63) found that the superior side of sumach leaves was considerably richer in tannin than the lower, the proportion in old leaves being less than in young. The results varied from 8·77 per cent. of tannin in the lower side of old, to 25·82 per cent. in the superior side of young leaves.

When applicable, the copper process has the advantage that the precipitate may be washed with a solution of ammonium carbonate, dried, and weighed. Or the precipitate may be ignited, the residue moistened with nitric acid, and re-ignited, and the cupric oxide weighed. Its weight, subtracted from the weight of the precipitate previously found, gives that of the tannic acid with which it was combined, or the latter may be found by multiplying the weight of CuO by 1·034. This factor probably applies only to gallotannic acid.

A. Carpené (*Jour. Chem. Soc.*, xxviii. 1054) recommends, for the determination of the tannin in *wine*, the use of a solution of ammonio-acetate of zinc containing a large excess of ammonia, which reagent has the property of forming with œno-tannin a tannate of zinc quite insoluble in water, in ammonia, and in excess of the reagent itself; while it gives no precipitate with alcohol, malic or tartaric acid, tartrates, glycerin, gelatin, albumin, or the iron salts of organic acids. With gallic and succinic acids, glucose, and salts of aluminium it forms precipitates soluble in excess of the reagent and in ammonia.

On treating the wine with an excess of ammoniacal zinc acetate, a precipitate is formed consisting of zinc tannate mixed with a small quantity of colouring matter. The wine is heated nearly to boiling to agglomerate the precipitate, which, after cooling, is filtered off and washed with a little boiling water, to remove adherent colouring matter. The precipitate is dissolved in dilute sulphuric acid, and the solution so obtained titrated with standard permanganate and indigo, as described on page 110. The results by this method are stated to be very accurate, when applied to wine, but Kathreiner found that with ordinary tannin-matters the figures were very inconstant.

DETERMINATION OF THE WEIGHT OF TANNIN ABSORBED BY HIDE.

Instead of precipitating or absorbing the tannin from an infusion by means of gelatin, and ascertaining the difference in the reducing power of the liquid before and after the operation, several operators have proposed to note the difference in the solid matter contained in the liquid. In doing this there is considerable practical difficulty. Thus the gelatinous matter must be so pure that it will not yield to water sufficient soluble matter to vitiate the result; the solution must be very dilute, or the whole of the tannin will not be absorbed; and special means must be taken to bring the gelatin in contact with the tannin, as otherwise the outer portions become swollen and impervious to the liquid, at least within any reasonable time. The last difficulty may be avoided by using finely-powdered hide to absorb the tannin, and adding it in small successive portions at intervals of ten or twelve hours, whereby the portions first added are made to do the greater part of the work, and the later additions effect the removal of the last of the tannin from the liquid. A more rapid plan is that of H. R. Procter, who operates as follows:—A piece of stout glass tube about 4 inches long and 1 inch in diameter (fig. 1), is fitted in one end with a perforated cork carrying a syphon tube, the larger leg of which is from 12 to 15 inches in length. The end of the shorter limb projects through the cork, and is covered with a little tuft of cotton wool and a piece of muslin to prevent the hide powder from passing into it. The wide tube is filled with about 5 grammes of hide powder, which is well shaken but not rammed in, and the open end is then covered by a circle of muslin, which is secured by an india-rubber band. The wide tube is then immersed in 100 c.c. of the tannin infusion (which should not contain less than 1 per cent. of tannin) contained in a beaker, and when the hide powder is thoroughly soaked the syphon is gently sucked so as to cause the liquid to pass over into a flask placed to receive it. When a volume of 50 c.c. has collected, it should be evaporated to dryness at 100° and the residue weighed. 50 c.c. of the original tannin infusion is similarly evaporated to dryness, when the difference between the weight of the two residues will be the weight of tannin, &c., absorbed by the hide from 50 c.c. of the infusion. The figure thus obtained requires to be corrected by the result of a blank experiment on hide and distilled water alone, for even the most carefully prepared hide gives a residue of 30 to 40 milligrammes from 5 grammes. This process, which is perhaps the most rational yet devised for assaying tanning materials, is unfortunately wanting in accuracy in presence of much gallic acid, which Procter found to be absorbed by hide from a 1 per cent. solution to an extent equal to 78 per cent. of the whole; an unstable compound with gelatin being apparently formed which in practical working would have been subsequently decomposed by the excess of tannin. Hence, for the assay of tanning materials containing much gallic acid, the oxidation method, in which a solution of gelatin is employed, is to be

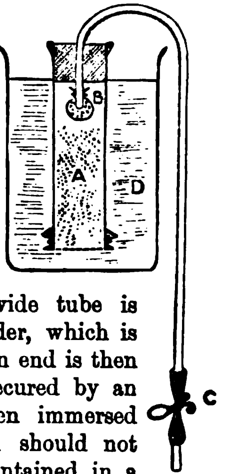


Fig. 1.

preferred to that of absorption by hide.[1] The hide process is in constant use at the Vienna *Versuchs-station für Leder-industrie,* where the error due to the presence of gallic acid has not been found of much practical moment. The rejection of the first 30 c.c. of the filtrate reduces it considerably, and also greatly lessens the effect of the soluble matter in the hide powder.

H. Dieudonné (*Jour. Soc. Chem. Ind.*, v. 549) has proposed to ascertain the density of the infusion before and after the absorption by means of a delicate hydrometer, instead of weighing the residues obtained on evaporating equal volumes to dryness. He uses a special hydrometer, on which 1° Baumé is divided into hundredths (!), and he gives a table of densities of solutions of gallotannic acid. The trifling saving of time effected by ascertaining the density of the infusions, instead of evaporating them to dryness, would be more than counterbalanced by the uncertainty that all tannins have the same solution-density as gallotannic acid.[2] The suggestion is practically a revival of the obsolete process of Hammer. According to this observer, for concentrations below 5 per cent., gallotannic acid has a solution-density of ·004. Above that strength the increase is slightly more rapid, a 10 per cent. solution having a density of 1·0406, and 15 per cent. of 1·0614, while a 20 per cent. solution has a density of 1·0824. Hence each 0·1 gramme of gallotannic acid present in 100 c.c. of its aqueous solution may be regarded as increasing the density by 0·0004.

Under ordinary circumstances, the direct observation of the increase in the weight of the hide, or other gelatinous substance employed, is impracticable, but purified catgut has been used, with apparent success, by A. Girard for the estimation of the tannin and colouring matter of *wine*[3] (*Jour. Soc. Chem. Ind.*, i. 464).

---

[1] According to T. C. Palmer (*Jour. Soc. Dyers, &c.*, iii. 175), sumach extracts give too high a result by the gelatin precipitation process, owing to the co-precipitation of pectinous matter. The error may be avoided by first dissolving the extract in alcohol, evaporating the filtered liquid, and redissolving the residue in water. With such treatment, at any rate if repeated, the precipitation process gives results agreeing with the absorption method.

[2] If any such method be adopted, the use of a Westphal balance is preferable to that of a hydrometer. By comparing the original and filtered infusion side by side far better results might be obtained, and if the experiments were accompanied by determinations of the solid matter corresponding to the densities observed, a useful series of tables might be constructed.

[3] Thick catgut (violin string) previously freed from oil by treatment with ether, is the best material to use, the quantity employed for 100 c.c. of wine being from 3 to 5 grammes, according to the character of the sample. The catgut is weighed, softened by soaking in water for five hours, and immersed in the wine for twenty or forty-eight hours, or until the liquid is completely

Other Methods of determining Tannins.

The direct weighing of the precipitate produced by gelatin in a solution of tannin was first suggested by Sir H. Davy, who stated that the precipitate contained 40 per cent. of gallotannic acid. The method has been more recently employed by Stoddart, Macagno, Günther, Johansen, Lehmann, and others, who differ widely in their statements as to the composition of the precipitate.[1] It undoubtedly varies greatly in composition according to the strength of the solution and other circumstances, besides which it is soluble in excess of gelatin solution and very difficult to wash free from alum or other salts employed to curdle it. The variable nature of the precipitate is liable also to vitiate the results obtained by employing a gelatin solution volumetrically, to say nothing of the difficulty of ascertaining the end of the reaction. But Lehmann has shown that the liquid may be diluted within certain limits without notably affecting the result, while the clarification of the liquid can be effected by adding powdered glass or barium sulphate, and vigorously stirring. He dilutes the tannin infusion with an equal volume of saturated aqueous solution of ammonium chloride, and titrates with a 1 per cent. solution of gelatin in cold saturated ammonium chloride. The end of the reaction is ascertained by filtering a few drops of the liquid and testing it with a solution of gelatin on a watch-glass placed on a black surface. *Catechu-tannic acid* is said to give good results in this way, 1 c.c. of the gelatin reagent representing 0·139 gramme of the tannin. Johansen recommends that a little chrome-alum should be added to the ammonium chloride solution.

A modified method of determining tannin by precipitation with

decolorised. The catgut is then removed, washed two or three times with water, pressed between folds of blotting paper, dried at 35° to 40° C. in an open dish, and afterwards at 100° in a vessel which can be closed. The increase in weight gives the quantity of colouring and astringent matters in the wine employed for the test. This process appears to be too slow for the assay of ordinary tannin-matters.

[1] Assuming the precipitate to contain 40 per cent. of tannin, Macagno obtained with sumach pretty constantly 53 per cent. of the results yielded by permanganate. Günther found that 100 parts of gelatin precipitated 77 of gallotannic acid, 132 of catechu-tannin, 130 of kino, 130 to 132 of ratanhia, 130 of oak-bark, or 168 of tormentilla-tannic acid. 100 parts of gelatin combined with 120 of dry gallotannic acid, according to Johansen, and with 130 of catechu-tannic acid according to Lehmann. Quite recently, C. Böttinger has found the precipitate produced by gallotannic acid to contain 16·5 per cent. of nitrogen, corresponding to 34 per cent. of tannin; while oak-bark tannin gave a precipitate containing 9·5 per cent. of nitrogen, corresponding to 42·7 per cent. of tannin (*Jour. Chem. Soc.*, liv. 614).

gelatin has been recently described by Collin and Benoist (*Jour. Soc. Dyers, &c.*, iv. 62), and appears to merit a careful trial. They employ an aniline dye in conjunction with gelatin, and operate in presence of calcium acetate.[1] The end of the operation is indicated by the decolorisation of the liquid, the dye being precipitated together with the gelatin.

A solution of tannin is made by dissolving 5 grammes of dry and absolutely pure tannic acid in water, adding 0·5 c.c. of a 10 per cent. solution of mercuric iodide dissolved in its own weight of potassium iodide, and diluting the liquid to 1 litre. A weight of 5 grammes of gelatin is dissolved in 1 litre of hot distilled water, the liquid boiled, and sufficient white of egg added to make it clear. After cooling, 0·5 c.c. of the mercuric iodide solution is added and sufficient caustic soda to render the liquid slightly alkaline. 50 grammes' weight of pure and dry calcium acetate is dissolved in 1 litre of water, and the filtered liquid treated with a few drops of the mercuric iodide solution. This appears to act as a perfect preservative of the solution, no alteration being perceptible even after four months.

For the assay of tannin infusions which are not coloured, a 1 per cent. solution of pure methylene blue is used. For coloured tannins or extracts either a 4 per cent. solution of Nicholson's blue BB, or a 1 per cent. solution of blue-black NBL.

For the determination a flask is used, having a capacity of about 60 c.c., and a neck 3 cm. in diameter. 1 c.c. of gelatin solution, two drops of blue solution and 5 c.c. of calcium acetate are measured into the flask, which is then filled to the neck with distilled water at a temperature of 75° to 80° C., by means of a burette capable of delivering at 40 drops to 1 c.c.[2] A little of the standard solution of tannin is added, when the flask is closed and shaken. A precipitate is formed which rapidly rises to the surface of the liquid, and the addition of the tannin is continued drop by drop with agitation between each addition until the solution becomes colourless. The process is then repeated with a solution of the tannin-matter to be assayed, which, if acid, should previously be nearly neutralised by the cautious addition of caustic soda.

---

[1] The use of magenta as an indicator was previously suggested by Wagner, but was found useless from the fact that it was freely absorbed by the precipitate of tannate of gelatin.

[2] The authors used specially constructed burettes. An ordinary burette with glass-tap would answer the purpose, if a special nozzle of drawn-out glass tube were attached to it by india-rubber tubing. Apparently it would not be difficult to modify the manipulation so as to employ larger quantities or more dilute solutions, and thus avoid the necessity of using a special burette.

The method has been tried under various conditions. Alterations in the strength of the tannin solutions; the presence of other organic matters, such as lactates, butyrates, gallates, and gallic acid; and all the salts that accompany tannin as it occurs in commerce, have little or no influence on the results. The operation is only spoilt when a large proportion of gallic acid is present, and this difficulty can be got rid of by adding a known measure of the standard tannin solution to the solution to be assayed, and subsequently making the requisite correction.

A method of assaying *tea*, originating with the author (*Chem. News*, xxix. 169, 189), was based on the precipitation of the tannin from a hot solution by a standard solution of lead acetate, the end of the reaction being ascertained by filtering a few drops of the liquid and testing it with ammoniacal ferricyanide (page 90). The method was selected partly because the indications included any gallic acid which might be present, and hence is not suited for the assay of tanning materials without some modification.[1]

R. Jackson (*Chem. News*, l. 179) has proposed to agitate tannin infusions with lead carbonate, filter after a few hours, and calculate the tannin from the loss of gravity, assuming a 1 per cent. solution of all kinds of tannin to be 1·0038.

In Gerland's process, the tannin is precipitated by a standard solution of tartar-emetic (2·611 grammes per litre), in presence of ammonium chloride, which prevents the co-precipitation of gallic acid. The assay of *sumach* by this method yielded J. Macagno results which were constantly two-thirds of those given by titration with permanganate. The tendency of the antimonial solution to change may be obviated by the addition of methylated spirit to the solution (or probably by carbolic acid). Some tannins (*e.g.*, those of catechu and horse-chestnut) are not precipitated by tartar-emetic.

Richards and Palmer (Silliman's *Amer. Jour. Science*, [3], xvi. 196, 361) substitute acetate for the chloride of ammonium in Gerland's process, and ascertain the point of complete precipitation of the tannin by testing a drop of the clear supernatant liquid on a hot porcelain plate with solution of sodium thiosulphate, which will produce an orange precipitate if the antimony is in excess.

---

[1] M. Villon (*Journ Soc. Chem. Ind.*, vi. 388) states that gallic acid is not precipitated by lead acetate, but the author has proved that only a minute trace remains in solution. It seems probable, as suggested by Guyard, that by using a solution of acetate of lead containing a considerable quantity of free acetic acid it might be possible to precipitate tannic acids (and colouring matter) while leaving gallic acid in solution, and then, by treating the lead precipitate with dilute sulphuric acid, a solution would be obtained in which the tannic acid could be determined by indigo and permanganate. This direction seems to the author the most hopeful one in which to work with a view of devising a rapid and direct process for the determination of tannins.

The estimation of tannin by precipitation with an ammoniacal solution of copper has already been described.

A. Casali (*Jour. Soc. Dyers, &c.*, i. 66) has proposed to determine tannin by precipitation with a solution of ammonio-sulphate of nickel. A volume of solution (1 c.c.) which will precipitate 0·01 gramme of gall-tannin is stated to be equivalent to 0·01497 of oak-bark tannin.

F. Becker has described a method of determining tannin by precipitation with a solution containing 5 grammes of methyl-violet per litre (*Jour. Soc. Dyers, &c.*, i. 180). 50 c.c. measure of this solution is diluted with 450 c.c. of water at 50° C., and a 1 per cent. solution of pure gallotannic acid run slowly in, with continual stirring, until the colouring matter is completely precipitated, a point readily ascertained by filtering a small sample. A similar experiment is then made with an infusion of the tanning material to be tested. The process is said to be well adapted for the assay of *sumach*, and would probably be found useful in most cases where the tannin is intended to be employed in dyeing.

Ostermeyer, improving on a suggestion of Wagner, has proposed to determine tannin by a standard solution of cinchonine coloured with magenta, the end of the reaction being indicated by the pink tint acquired by the solution (*Chem. News*, xl. 181). Gallic acid is not precipitated by cinchonine. Some observers report unfavourably of this process, and state that in certain cases the liquid acquires a red tinge long before the tannin is precipitated.

F. Jean (*Jour. Soc. Chem. Ind.*, v. 179) has described an ingenious process of determining tannin, based on the volume of the infusion requisite to render a solution of iron opaque. The operation is conducted in a beaker 8½ centimetres in diameter, placed in a good light on a black cloth, having on it a small circle of white paper about 5 cm. in diameter. 5 c.c. measure of a solution of iron, containing 14 grammes of ferric chloride and 10 c.c. of hydrochloric acid per litre, is run into the beaker, and 200 c.c. of water added. A 0·1 per cent. solution of tannin is then dropped in with constant stirring. The operation is finished when the disk of white paper is wholly invisible after the liquid has come to rest, which in the case of pure gallotannic acid occurs when 11·6 c.c. of the solution has been added. In comparing tanning materials with this it is simply necessary to take care that the infusions are approximately of the same richness in tannin, and this may be attained by extracting 1·5 gramme of European bark, 1·0 of African bark, 0·5 of Quebracho, 0·5 of sumach, or 0·25 gramme of catechu, and diluting the liquid to 100 c.c. The determination can be made very rapidly, and is said to be accurate to ½ per cent. By subsequently repeating the experiment with a solution which has been treated with hide, the error caused by gallic acid may be eliminated.

E. Durien (*Year-Book Pharm.*, 1886, iii.) has proposed to determine tannin by adding acetic acid and ferric chloride to the infusion, and then dropping in a standard solution of bleaching powder (5 grammes per litre) till the colour of the liquid changes suddenly to a rose-brown tint. Sugar was found not to affect the result, but gallic acid is ignored.

F. Musset (*Chem. News*, li. 42) has described a method of titrating tannin by oxidation with iodine. 100 c.c. of a 1 per cent. of bark is treated with 20 c.c. of decinormal solution of iodine (12·7 grammes per litre), the flask filled to the neck with warm air-free water, and carefully closed. After twelve hours, the free iodine is reduced by standard thiosulphate solution, which should be added somewhat in excess, and the liquid titrated back with decinormal iodine and starch. By operating in a similar manner on a solution which has been treated with gelatin, the disturbing effect of gallic acid and other "not tannin" matters is ascertained, and can be allowed for.

EXAMINATION OF TAN-LIQUORS.

Besides determining the tannin and oxidisable substances in tan-liquors, it is frequently desirable to obtain further information as to the proportion and nature of the free acids present. It is an error to suppose that the principal free acid of tan-liquors is gallic acid, as this is not present in pure bark-yards. The most abundant acid is usually acetic, though butyric, lactic, and other acids produced by fermentation are frequently present.

The total free acid may be ascertained by titrating the filtered liquid (previously clarified, if necessary, with kaolin) with lime-water. The end of the reaction is indicated by the production of a permanent turbidity, showing that the acids which held the calcium tannate in solution are neutralised. By titrating another portion of the liquor with lime-water, using methyl-orange as an indicator, the proportion of strong acids capable of producing "plumping," or swelling of the leather, will be roughly ascertained. Sulphuric acid is sometimes added for this purpose.

A more accurate and elaborate method of assaying tan-liquors has been described by Kohnstein and Simand (*Jour. Chem. Soc.*, xlviii. 935). To determine the *volatile organic acids* (acetic, butyric, &c.), 100 c.c. measure of the liquor is distilled to

30 c.c., the residue made up with water to the original bulk and again distilled, and the process repeated till the total distillate measures 300 c.c., when it is titrated with standard caustic alkali and phenolphthaleïn, and the acidity expressed in terms of acetic acid. By adding sulphuric acid and water to the contents of the retort, and again distilling and titrating the distillate, the combined acetic acid may be determined.

Another portion of the liquid (80 or 100 c.c.) is shaken with 3 to 4 grammes of freshly-ignited magnesia, quite free from carbonate and lime. The mixture is left for some hours with frequent agitation, when the brown or dirty green colour will have disappeared, and the filtered liquid will be nearly colourless, neutral, and free from tannin. The magnesia in solution is determined in an aliquot part of the filtered solution, and will be equivalent to the total free acids of the liquor, exclusive of the tannic acid, which is completely precipitated together with the colouring matter. Another portion of the filtrate is evaporated to dryness, and the residue *gently* ignited. The ash is moistened with carbonic acid water and dried. It is then boiled with distilled water, and the solution filtered. The magnesia remaining insoluble corresponds to that which existed in the solution as magnesium salts of *organic acids*, and may be determined gravimetrically as pyrophosphate, or dissolved in standard acid and titrated with alkali and methyl-orange or litmus. By dividing the percentage of acetic acid previously found by 3, and subtracting this figure from the percentage of MgO, the weight of the latter corresponding to the *non-volatile organic acids* of the liquor will be found; and 4·5 times this amount will be their equivalent of lactic acid. The magnesia contained in the aqueous solution of the ash is equivalent to the free *sulphuric acid* originally present.

The liquors of a set of seven handlers, in a Continental upper-leather tannery in which larch-bark was used, showed, by the above process, in grammes per 100 c.c.:—Total acids reckoned as acetic, from 0·20 to 0·68; volatile acids, 0·05 to 0·46; and fixed organic acids reckoned as lactic acid, 0·05 to 0·59.

Writing Inks.

Writing inks are either coloured liquids, or liquids containing a finely-divided precipitate in suspension.

Ordinary writing ink was formerly always made from a decoction of galls, to which green vitriol was added. Of late, the composition of writing inks has become far less constant, aniline and other dyes being frequently employed, and other metallic salts substituted for the ferrous sulphate formerly invariably used.

The table following shows the general composition of black writing inks, and sufficiently indicates the nature of the substances to be sought for by the analyst:—

	Superior Ink.	Inferior Ink.	Ink containing Vinegar.	Logwood Ink.	Copying Ink.	Copper Ink.	Runge's Chrome Ink.	Copying Ink.	Ink Powder.	Stephen's Blue-black Ink.
Galls, . . .	225	62	174	50	60	42	...	...	12	15
Logwood, . .	...	...	...	100	21	20	140	4	...	...
Potassium chromate, . .	...	...	...	...	...	...	1	...	...	...
Ferrous sulphate,	75	81	87	16	20	21	...	3	5	5
Cupric sulphate,	...	...	...	...	...	5	...	...	...	4 iron filings.
Alum, . .	...	...	...	...	...	...	...	2	...	...
Gum, . . .	25	81	48	47	20	16	...	3	2	...
Sugar, . .	...	...	...	28	1000(?)	...	...	5	1	...
Vinegar, . .	...	...	135	...	...	...	...	60	...	...
Water, . .	1000	1000	1000	...	1000	1000	1000	70	...	200 ½ indigo in 8 of sulphuric acid.

The best black ink is a tanno-gallate of iron, obtained by adding an infusion of nut-galls to a solution of ferrous sulphate (copperas). The galls contain gallic and gallotannic acids, both of which are serviceable. On coming in contact with ferrous salts in concentrated solutions, these produce white precipitates which turn black on exposure to air. With ferric salts, blue-black precipitates are at once produced. A small quantity of gum is added to retain the precipitate in suspension. To ink intended for copying by pressure a small addition of sugar or glycerin is also made.

Sumach is sometimes used instead of galls, and some of the nut-gall inks contain a little acetic acid, added as vinegar.

Some of the gallic inks receive an addition of indigo-carmine or sulphindigotic acid. Aniline dyes are frequently used as a whole or part of the colouring matter of both black and coloured inks.

According to R. Böttger, an excellent black ink may be prepared by dissolving in water 1 part of pyrogallol, 3 of ammonium vanadate, and 3 of finely powdered gum-arabic. Another highly recommended ink is made with nigrosine (an aniline black), potassium bichromate, and gelatin.

Logwood is a frequent constituent of ink. It gives the original ink a darker hue, and itself contains tannin, besides the colouring matter hæmatoxylin. Logwood and alum form a frequent basis of purple inks.

A very cheap and perfect ink is obtained by dissolving 24 parts of extract of logwood in 1000 of water, and adding 2 parts of neutral potassium chromate. This ink is a deep black liquid, which, unlike that made with gallic acid and iron, contains no deposit.

Sulphate of copper is sometimes added to ink, with questionable advantage.

Indelible ink usually owes its permanency to an admixture of finely-divided carbon, to which indigo is sometimes added. It is kept in suspension by gluten, an alkaline solution of shellac, or other similar means.

In analysing ink, the *total solid residue* should be determined by evaporating 50 c.c. to dryness on the water-bath. The residue thus obtained is first weighed and next ignited, the odour produced on heating being carefully noted; sugar or shellac may thus be detected. The weight of the ignited residue is then taken, after which it is mixed with magnesia and caustic soda, and ignited in platinum. The mass is extracted with hot water, the solution filtered, and the filtrate acidulated with acetic acid. In presence of a chromate, the liquid will have a yellow colour, and will give a chrome-yellow precipitate on adding acetate of lead. The precipitated $PbCrO_4$ may be collected and weighed, or the chromate formed determined volumetrically by a ferrous salt. The residue left on treating the fused mass with water should be boiled with hydrochloric acid, the liquid filtered and examined for iron, copper, aluminium, &c., in the usual way. By precipitating the solution with a large excess of ammonia, the iron and aluminium may be roughly separated from the copper, which remains in solution and communicates a blue colour to the liquid.

For the detection of *organic colouring matters*, a portion of the ink should be strongly acidulated with hydrochloric acid. A blue colour, unaffected by the acid, but destroyed on adding bromine water or bleaching powder, shows the presence of indigo. If prussian blue be present, the ink will probably turn brown on addition of soda, and the filtered liquid will give a deep blue precipitate with ferric chloride, after being acidified with hydrochloric acid. A black colour, not destroyed by acids or alkalies, nor bleached by chlorine or bromine, is pretty certain to be due to finely-divided carbon. An ink prepared with ammonium vanadate and galls is turned blue by acids, but is unaffected by alkalies. Its colour is altered but not bleached by chlorine. Aniline-black is not affected by alkalies, but is turned dark green by acids; bleaching powder renders it garnet-red. Logwood inks are turned red or yellow by hydrochloric acid, while those containing galls only are almost wholly decolorised by the same reagent.

Some inks have a great tendency to become mildewed; this may be prevented by a small addition of carbolic or salicylic acid. Essential oils are sometimes used for the same purpose.

COLOURED INKS do not usually contain tannic acid, and hence their discussion is out of place in this section; in many instances they are nothing but solutions of coal-tar dyes. The following examples will suffice to give a general idea of their composition:—

Red.—Brazil wood, with stannous chloride or cream of tartar and alum; cochineal or carmine dissolved in ammonia or sodium silicate; aniline red.

Blue.—Prussian blue dissolved in oxalic acid; aniline blue.

Violet.—Aniline violet.

Green.—Acetate of copper and cream of tartar; chrome alum; iodine green.

MARKING INKS are all closely analogous in composition, and their assay requires no special description. They usually consist of nitrate of silver coloured with sap-green, ivory-black, indigo, &c.; or ammonio-nitrate of silver mixed with sodium carbonate, sometimes with sulphate of copper added. In Redwood's ink, tartrate of silver is substituted for the nitrate. Reade's ink is ammonio-tartrate of silver.

PRINTING INK is made by suspending lampblack in linseed oil, with more or less rosin oil, rosin, turpentine, &c.

CHEMICAL EXAMINATION OF INK MARKS.

In chemico-legal cases it is sometimes of importance to ascertain the nature of the ink used, to compare it with specimens of writing of known history, and to ascertain the relative ages of the writings. A minute inspection should first be made with a magnifying power of about 10 diameters, and any peculiarities of colour, lustre, shade, &c., duly noted, and where lines cross each other which lie uppermost. The examination is often facilitated by moistening the paper with benzene or petroleum spirit, whereby it is rendered semi-transparent. The use of alcohol or water is inadmissible.

Valuable information is often obtainable by treating writing or other ink-marks with reagents. Some inks are affected much more rapidly than others, though the rate of change depends greatly on the age of the writing. Normal oxalic acid (63 grammes per litre), or hydrochloric acid of a corresponding strength, should be applied to a part of the ink mark with a feather or camel-hair brush (or the writing may be traced over with a quill pen), and the action observed by means of a lens, the reagent being allowed to dry on the paper.[1] Recent writing (one or two days old) in gallic inks is changed by one application of oxalic acid to a light grey, or by hydrochloric acid to yellow. Older stains resist longer, in proportion to their age, and a deeper colour remains. Logwood ink marks are mostly reddened by oxalic acid, and alizarin marks become bluish, but aniline inks are unaffected. With hydrochloric acid, logwood ink marks turn reddish or reddish-grey, alizarin marks greenish, and aniline ink marks reddish or brownish-grey. The treatment with acid should be followed by exposure to ammonia vapours, or blotting paper wet with ammonia may be applied. Thus treated, marks in logwood ink turn dark violet or violet-black. The age of ink marks very greatly affects the rate of their fading when treated with dilute ammonia, the old marks being more refractory. The behaviour of ink marks when treated with solution of bleaching powder is often characteristic, the older writings resisting longer, but unless the reagent be extremely dilute, writings of all ages are removed almost simultaneously (R. Irvine, *Jour. Soc. Chem. Ind.*, vi. 807). Hydrogen peroxide acts more slowly than bleaching solution, but gives more definite results. After bleaching the mark by either reagent, the iron of the ink remains mordanted on the paper, and the mark may be restored by treatment with a dilute solution of galls, tannic acid, or acidulated potassium ferrocyanide. The same reagents may be used for restoring writing which has faded from age alone.

---

[1] The author succeeded by this treatment in detecting an alteration in a receipt on account in which a figure 1 had been altered to 4. The added mark, as also a forged signature across the stamp necessitated by the change, faded out first under treatment with dilute hydrochloric acid.

Where ink marks have been erased or discharged by chemical means, traces of the treatment are often recognisable. After effecting the erasure, the spot is often rubbed over with powdered alum or gum sandarac, or coated with gelatin or size. The bleaching agents most likely to have been used are oxalic, citric, or hydrochloric acid, bleaching powder solution, or acid sulphite of sodium. Moistened litmus paper will indicate the presence of a free acid, and in some cases treatment with ammonia fumes will restore the colour. The presence of calcium, chlorides, or sulphates in the water in which the paper is soaked will afford some indication of bleaching powder or a sulphite having been used. Potassium ferrocyanide will detect any iron remaining in the paper. Exposure to iodine vapour often affords evidence of chemical treatment, and other methods of examination readily suggest themselves.

The application of reagents to writing in black ink has been recommended by W. Thomson for the identification of handwriting (*Chem. News*, xlii. 32).

DYES AND COLOURING MATTERS.

UNTIL the middle of this century, nearly all the colouring matters used for dyeing were either such as existed ready-formed in the vegetable or animal kingdom, or were producible from natural products by very simple chemical processes. In a few cases, however, as when chromate of lead or prussian blue was formed as an insoluble precipitate in the fibre, the dyes were strictly of artificial origin. Now, the vast majority of the colouring matters used as dyes—as distinguished from mere paints or pigments—are products of organic synthesis, being in almost all cases obtained, by a series of highly scientific processes, from coal-tar.[1]

---

[1] Picric acid and aurin are the oldest of the coal-tar colours, but the coal-tar colour industry may be said to date from 1856, when Perkin accidentally discovered the violet dye called mauve, in the course of an investigation having as its object the synthesis of quinine. In 1860, rosaniline or magenta first became of commercial importance, owing to the simultaneous discovery of the arsenic acid process by Medlock and Nicholson. Phenylated blues were first produced by Girard and De Laire in the same year, but their insolubility rendered their application limited until Nicholson, in 1862, discovered a method of rendering them soluble by conversion into sulphonic acids. The first azo-dye, amido-azobenzene, was introduced by Simpson, Maule, & Nicholson in 1863, under the name of aniline yellow, and in the same year the methylated and ethylated rosanilines, known as Hofmann's violets, were manufactured by the same firm. Aniline black, also, was discovered by Lightfoot in 1863. Azo-diphenyl blue, the first of colouring matters now known as indulines, appeared in 1864, as also did dinitronaphthol or Manchester yellow. In 1866, triamido-azobenzene or Bismarck brown was first made, and in the same year Coupier's nitrobenzene process of manufacturing magenta was introduced. In 1868, Graebe and Liebermann announced their discovery of the constitution of alizarin, and in the following year this colouring matter was first manufactured from anthracene. Galleïn and fluoresceïn were discovered in 1871, and in 1874 tetrabromfluoresceïn was introduced as a dye by Caro, under the name of eosin. Diamido-azobenzene or chrysoïdine was introduced by Witt in 1875. Methylene blue and acid magenta were introduced by Caro in 1877, and in the same year the fugitive aniline yellow was rendered valuable and stable by Grässler, by conversion into a

The term aniline dye is in popular phraseology regarded as synonymous with coal-tar dye, but this definition is far from accurate. Picric acid and its allies, aurin, the various eosins, alizarin and anthrapurpurin, indigo, and many other important colouring matters are now strictly coal-tar dyes, though they cannot by any straining of the term be appropriately described as aniline dyes.

Graebe and Liebermann have enunciated the rule that all coloured organic compounds (*e.g.*, quinones, azobenzene derivatives, nitro-compounds, &c.) are decolorised by reducing agents, and from this they infer that the colouring matters either contain elements with incompletely saturated affinities, or that certain of the atoms are present in more intimate association than their retention in the molecule necessitates. O. Witt has formulated the conclusion that the tinctorial nature of aromatic compounds is the consequence of the presence together of a colour-giving or chromophoric group, such as NO_2, CO, or N : N, and a salt-forming group, either OH or NH_2. The common proposition that all bodies containing, for instance, an NO_2 and an OH group are coloured, does not hold true. Upon the nature of the salt-forming group depends the character of the colouring matter, those containing OH being usually acids, while all basic colouring matters contain at least one NH_2 group, either intact or substituted.

Basic Colouring Matters are always employed in dyeing in the form of one of their salts, the hydrochloride being the usual form of combination, though the acetate, nitrate, and other compounds are employed in certain cases. Colouring matters of distinctly basic character, which lose their colour on coming in

sulphonic acid. In 1878, the tropæolins, fast-red, naphthol-scarlet, and other sulphonated azo-colours were first manufactured; and malachite green dates from the same year. In 1879, the first of the secondary azo-dyes appeared under the name of Biebrich scarlet. The analogous crocein scarlets, discovered in 1881, are fast exterminating the cochineal industry. The synthesis of indigo was effected by Baeyer in 1880, and indophenols were introduced by Koechlin and Witt in 1881. In 1883, Caro's process of manufacturing colouring matters of the rosaniline group by the aid of phosgene gas was patented. Congo-red, the first of the numerous class of benzidine dyes, which dye cotton without a mordant, was patented by Böttger in 1884, and this was followed in the same year by chrysamin. In 1885, azo-blue and benzazurin appeared, and in 1886 the benzopurpurins were patented. Numerous other dyes are constantly appearing, and in many cases they exceed in fastness, brilliancy, or cheapness those already in the market. (For an interesting paper by R. Meldola, from which most of the above information is derived, see *Jour. Soc. Arts*, May 28, 1886; or *Jour. Soc. Dyers, &c.*, ii. 95.)

contact with acids, cannot be employed in dyeing, except certain very weak bases, which are absorbed by the fibre as such, and not in the form of their salts. Amido-azobenzene (aniline yellow) is an instance of this, for its salts are decomposed by water, and hence, when silk is dyed by an acidulated solution of its hydrochloride, and is then washed with water, the free base only remains on the fibre. In the free state, the colour-bases are usually colourless, or only slightly coloured. Most of them can be converted into soluble acid colouring matters (sulphonic acids) by treatment with strong sulphuric acid.

ACID COLOURING MATTERS, like all acids, contain hydrogen which is readily replaceable by metals with formation of salts. The hydrogen may form part of a hydroxyl group, OH, as in picric acid; of a sulphonic group, SO_3H, as in helianthin; of an imido group, NH, as in aurantia; or of a carboxyl group, COOH, as in the scarlet obtained from salicylic acid. Those colouring matters which owe their acid properties to the hydroxyl group are very weak acids (*e.g.*, alizarin, aurin); but the acid characters are considerably intensified by the introduction of haloid or nitro-groups. Thus the eosins and nitrophenols have much stronger acid characters than the fluoresceïn and phenol from which they are derived. The acid colouring matters (excepting sulphonic acids) are insoluble or only sparingly soluble in water, but dissolve in dilute alkalies. In other words, their alkali-metal salts are soluble, and this solubility increases with the number of hydroxyl groups, but if the hydrogen of the OH be replaced by alkyl radicals, the resultant compounds are rendered less soluble or insoluble in water. Many of the acid colouring matters unite with metallic hydroxides (*e.g.*, stannic, ferric, chromic, aluminic) to form insoluble compounds called lakes.

SULPHONIC ACIDS may be derived from either basic or phenolic colours, and are obtainable either by the action of sulphuric acid on a ready-formed colouring matter, or by the direct transformation of a previously prepared sulphonic acid into a colouring matter. The sulphonic group, SO_3H, is not a chromophore, and has so little influence on the colour that the original and the sulphonated dye are usually of exactly the same colour. The sulphonic acids are usually soluble, and can be employed in acid baths, and volatile colouring matters (*e.g.*, aniline yellow) can be rendered non-volatile by sulphonation. The salts of the sulphonic acids are generally soluble. Those derived from azo-dyes have usually the colour of the free sulphonic acids, and are taken up by the fibre as salts; while the salts of the sulphonated basic dyes have usually a dull, indefinite colour, and in these cases it is the free sulphonic acid which is taken up by the fibre, or rather which is retained by it. Thus, alkali-blue is absorbed by the fibre as a salt, the free sulphonic acid being subsequently liberated by immersion in an acid bath.

NEUTRAL COLOURING MATTERS are rarely met with. Indigo is the most notable example, but the special means employed in using it sufficiently indicate its exceptional character.

Relations of Colouring Matters to Fibres.

While the chemist defines dyes and colouring matters as acid, basic, and neutral, the dyer classifies them according to their behaviour with fibres. Thus, excluding indigo, aniline black, prussian blue, and a few other colouring matters which are produced by some chemical reaction occurring within the fibre itself, dyes may be classed as substantive and adjective.

SUBSTANTIVE DYES are absorbed directly from their solutions by the fibre, and combine with it without requiring the intervention of a mordant. The animal fibres (*e.g.*, silk and wool) possess great affinity for most of the coal-tar colours, and in many cases absorb them so completely that the liquid is rendered colourless. Many colouring matters are taken up by animal fibres more readily from an acid than from a neutral bath; and in such cases the bath is usually acidified ("soured") by sulphuric, acetic, or tartaric acid. If sulphuric acid be used, sodium sulphate is generally added also, as the resultant acid sulphate of sodium has less action on the fibre than free sulphuric acid. Some dyers add acid sodium sulphate as such, instead of forming it in the dye-bath.[1] In wool-dyeing, sodium or magnesium sulphate is often added to the bath, to reduce the solubility of the colouring matter, and obtain faster and more even colours. In order to avoid an uneven or "cloudy" appearance, silk is usually dyed in a weak soap-bath made with Marseilles or good olive-oil soap. If an acid bath is required, boiled-off liquor is used, together with sulphuric or acetic acid.

It is generally assumed that in substantive dyeing a chemical combination ensues between the colouring matter and the fibre. But in some cases, as when wool is dyed with alkali-blue or cotton with indigo, a colourless neutral substance is absorbed by the neutral and indifferent fibre, and is only converted into a coloured body by a subsequent chemical reaction, namely, the liberation of the free sulphonic acid in the first case, and oxidation to indigo-blue in the latter.

The "ingrain colours" produced on cotton by means of primulin afford a remarkable example of the building up of a dye within the fibre.

---

[1] Care must be taken not to employ the impure acid sodium sulphate known in commerce as "nitre-cake," as nitric acid has a very injurious action on many colouring matters.

Cotton shows but little tendency to combine with coal-tar dyes, except these known as the benzidine colours, which dye it without requiring the agency of a mordant. On the other hand, oxycellulose, vegetable parchment, and the various modifications of nitrocellulose possess considerable affinity for coal-tar colours.

ADJECTIVE DYEING. MORDANTS.—In the great majority of cases, cotton and other vegetable fibres can only be dyed through the intervention of a mordant. Sometimes the mordant acts by forming an insoluble compound with the colouring matter, according to a definite chemical reaction; and in other cases simply serves as a medium on which the colour acts as a substantive dye. Albumin acts in this way, as also many substances in a state of fine division, such as calcium phosphate and carbonate, silica, &c., when precipitated on the fibre. In some cases, colouring matters which have themselves been fixed on the fibre act as mordants for others. Thus the benzidine dyes may be employed for mordanting the basic aniline dyes on cotton. Several useful combinations are thus obtainable.

The proteïds resemble silk and wool in their affinity for coal-tar dyes, and hence albumin, &c., are employed in calico-printing. A solution of albumin mixed with the colouring matter is printed on the cotton fibre. On steaming, the albumin is coagulated and the colour becomes fixed.

Tannin acts as a mordant for basic dyes, as it forms with them insoluble tannates.[1] These compounds are soluble in acetic acid or alcohol, and if the solutions thus obtained are thickened with starch or dextrin and printed on cotton, the tannate becomes fixed and insoluble on steaming the goods. Better results are obtained by employing in conjunction with the tannin and colour-base a metallic salt (*e.g.*, tartar emetic, stannic chloride, lead acetate, &c.) capable of reacting to form an insoluble tannate.

The use of oil in dyeing turkey-red is a familiar example of the application of oil mordants, which are generally employed in conjunction with inorganic mordants.

---

[1] The tannates of the colour-bases may be either soluble or insoluble, according to the proportions used, the following being the quantities required to form insoluble lakes, according to J. Koechlin:—

	Dye.	Tannic Acid.	Soda Crystals.
Magenta, . .	4	5	2
Malachite green, .	4	5	1
Parma, . . .	4	5	1
Methyl green, .	4	10	4

Silica, sulphur, and metallic ferrocyanides and sulphides (*e.g.*, of zinc and tin) act as useful mordants for certain dyes.

On soda being added gradually to a solution of lead acetate or aluminium sulphate, avoiding the formation of an actual precipitate, a basic compound is formed which is decomposed by cotton fibre into a still more basic one which remains fixed and insoluble, and a soluble acid salt. The complete fixation of the mordant can be effected by immersing the cotton in a dilute solution of soap or alkaline carbonate, or by washing it with hard water. Wool has a greater affinity than cotton for metallic hydroxides, and hence alum is partially decomposed by wool with liberation of sulphuric acid. Chemical equilibrium is soon reached, but if a tartrate be added the absorption of alumina proceeds much further, as tartaric acid is liberated instead of sulphuric acid.

The acetates of iron (ferric), aluminium, and some other metals undergo decomposition when heated, with formation of free acetic acid and insoluble basic acetates. Hence these metallic acetates act as valuable mordants which become perfectly fixed by steaming. The thiocyanates have recently come into use for a similar purpose.

Classification of Dyes and Colouring Matters.

The arrangement of dyes and colouring matters in groups with a view to their convenient description is preferably based on their chemical characters. In certain cases, however, the dyes defy simple classification, and in others a strict adherence to a system produces inconvenience. The colouring matters still obtained from natural sources are also best considered in the same section, however different they may be in chemical nature.

The following arrangement is that adopted in this work for the description of the dyes and colouring matters and the methods of recognising them :—

1. Nitro-colouring matters.—*Example.* Picric acid.
2. Nitroso-colouring matters.—*Ex.* Resorcin green.
3. Aurin and its allies.—*Ex.* Rosolic acid.
4. Phthaleïns.—*Ex.* Eosin. Galleïn.
5. Azo-colouring matters.—*Ex.* Helianthin. Congo-red.
6. Rosaniline and its allies.—*Ex.* Hofmann's violet.
7. Safranines and Indophonols.
8. Colouring matters from anthracene.—*Ex.* Alizarin.
9. Sulphuretted and unclassified coal-tar dyes.
10. Colouring matters of natural origin—*Ex.* Archil. Indigo.
11. Recognition of dyes and colouring matters.
12. Examination of commercial colouring matters.
13. Examination of dyed fibres.

NITRO-COLOURING MATTERS.

Nitric acid acts very violently on phenol and similar bodies, and by the direct reaction or indirect means a number of bodies may be obtained, some of which are colouring matters of considerable commercial importance.

The resulting nitro-compounds contain one or more atoms of the radical nitryl, (NO_2), in place of the hydrogen of the original substance. They are crystalline bodies, usually more or less yellow in colour, only slightly soluble in cold water, and not soluble to any great extent in boiling water; but they are readily soluble in alcohol and ether, and are removed by the latter solvent from their acidulated aqueous solutions.

The nitrophenols and their allies have marked acid properties, readily decomposing metallic carbonates, and furnishing a series of salts all or nearly all of which are more or less soluble in water, and often form crystals of great beauty, ranging in colour from a pale yellow to a fine crimson. The salts of the nitrophenols and their allies all deflagrate with greater or less facility when ignited, and many of them detonate on percussion, the more highly nitrated compounds (*e.g.*, the picrates) exploding with considerable violence (page 141).

In cases where the nitro-body is the product of a limited nitration, it may be converted into the corresponding sulphonic acid by treatment with strong sulphuric acid; but this is not possible when, as in the case of picric acid, the number of nitryl atoms in the molecule is at the maximum. The sulphonic acids of the nitro-colouring matters are stable bodies, readily soluble in water. The nitro-colouring matters as a class dye wool and silk yellow or orange, but have no affinity for cotton. Their acid characters are well marked and stronger than the phenoloïd bodies from which they are derived. They dissolve in concentrated sulphuric acid to form yellow or colourless solutions. Strong reducing agents, such as stannous chloride and hydrochloric acid, convert them into the colourless amido-derivatives. Fibres dyed with nitro-colouring matters, or aqueous solutions of the bodies themselves, are but slightly altered by hydrochloric acid, while ammonia and caustic soda tend to darken or redden the colour. With fibres dyed by nitro-colouring matters in acid baths, the colour may subsequently be partly removed by boiling water. These reactions serve to distinguish the nitro-dyes from other yellow colouring matters. Thus phosphine is turned lighter, while the yellow azo-dyes are reddened by acids. Phosphine, again, is extracted from its alkaline aqueous solutions on agitation with ether, but the nitro-compounds are not dissolved by ether under similar conditions. In presence of dilute sulphuric acid in excess, the simple nitro-dyes (*e.g.*, picric acid, dinitrocresol, dinitronaphthol, and aurantia) are extracted by ether, but the sulphonic acids (*e.g.*, naphthol yellow S) are not dissolved, in this respect resembling the yellow azo-dyes (except chrysamin).

The following is a list of the principal nitro-colouring matters:—

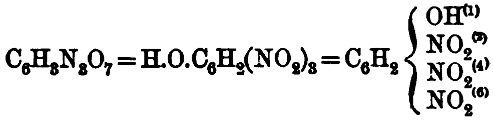
Commercial Name.	Chemical Name or Nature.	Formula.	Dyes Silk.
Picric acid. (Page 139.)	Symmetrical Trinitrophenol.	$C_6H_2\left\{\begin{array}{l}OH^{(1)}\\NO_2^{(2)}\\NO_2^{(6)}\\NO_2^{(4)}\end{array}\right.$	Greenish-yellow.
Flavaurin. (Page 151.)	Ammonium salt of Dinitrophenol-parasulphonic acid.	$C_6H_2\left\{\begin{array}{l}O(NH_4)^{(1)}\\NO_2^{(2)}\\NO_2^{(6)}\\SO_3(NH_4)^{(4)}.\end{array}\right.$	Yellow.
Victoria yellow; Aniline orange; Saffron substitute; Gold yellow.	Mixture of K or Na salts of Dinitro-ortho- and para-cresols.	$C_6H_2\left\{\begin{array}{l}OK\\NO_2\\NO_2\\CH_3\end{array}\right.$	Bright yellow.
Manchester yellow; Martius' yellow; Naphthalene yellow; Naphthylamine yellow.	Na, K, or Ca salt of Dinitro-alphanaphthol.	$C_6H_4\left\{\begin{array}{l}C(ONa):C(NO_2)\\\quad\quad\quad\quad\;\;\vert\\C(NO_2):CH.\end{array}\right.$	Bright yellow.
Naphthol yellow S.; Naphthol yellow; Acid yellow S.; Brilliant yellow. (Page 154.)	Sodium or other salts of Dinitro-alphanaphthol-sulphonic acid (or the free acid).	$C_6H_3(SO_3Na)^{\beta}\left\{\begin{array}{l}C(ONa):C(NO_2)\\\quad\quad\quad\quad\;\;\vert\\C(NO_2):CH.\end{array}\right.$	Yellow.
Citronin. (Page 156.)	Tetranitro-diphenylamine (with a little of the dinitro-compound).	$NH\left\{\begin{array}{l}C_6H_3(NO_2)_2\\C_6H_3(NO_2)_2.\end{array}\right.$	Yellow.
Aurantia; Blackley orange; Imperial yellow. (Page 156.)	Ammonium salt of Hexanitrodiphenylamine.	$N(NH_4)\left\{\begin{array}{l}C_6H_2(NO_2)_3\\C_6H_2(NO_2)_3.\end{array}\right.$	Orange.

Besides the colouring matters in the foregoing table, the following obsolete or nearly obsolete dyes belong to the nitro-group:—

Commercial Name.	Chemical Nature.	Formula.	Characters and Mode of Formation.
Phenyl brown; Phénicienne.	Contains Dinitrophenol and other bodies.	...	Yellow-brown powder produced by action of nitric acid on crude-phenol. Melts at gentle heat and deflagrates on further heating. Only partly soluble in water. Alkalies turn solution bluish-violet.
Palatine orange	Ammonium salt of Tetranitrodiphenol.	$\left\{\begin{array}{l}C_6H_2(NO_2)_2.O(NH_4).\\C_6H_2(NO_2)_2.O(NH_4).\end{array}\right.$	Soluble brown powder produced by action of nitric acid on benzidine. Does not deflagrate on heating. Acids precipitate brown flakes, melting at 220°.
Heliochrysin; Sun-gold.	Na salt of Tetranitroalphanaphthol.	$C_{10}H_3(NO_2)_4.ONa^{\alpha}.$	Brilliant yellow; very fugitive.

The following sections contain detailed descriptions of the principal nitro-colouring matters.

Picric Acid. Para-diortho-trinitrophenol. Trinitrophenic Acid.



$$C_6H_3N_3O_7 = H.O.C_6H_2(NO_2)_3 = C_6H_2 \left\{ \begin{array}{l} OH^{(1)} \\ NO_2^{(2)} \\ NO_2^{(4)} \\ NO_2^{(6)} \end{array} \right.$$

This substance, formerly called carbazotic acid, is the final product of the action of nitric acid on a large number of substances containing a benzene nucleus, just as oxalic acid is the result of the oxidation of many bodies of the fatty series. Picric acid is obtainable from indigo, aloes, gum-resins, wool, silk, &c.

Picric acid was formerly prepared by the direct action of nitric acid on phenol, but is now made by first dissolving the phenol in strong sulphuric acid and then acting on the resultant phenol-sulphonic acid by excess of nitric acid.[1] Mono- or dinitro- phenol may result if the action be not carried sufficiently far.[2] According to T. Whitaker (*Jour. Soc. Dyers, &c.*, iv. 87), if the sulphuric acid used for sulphonation contain nitrous compounds the picric acid has a brownish colour instead of being pure yellow.

---

[1] Picric acid is now manufactured on a large scale by mixing equal parts by weight of crystallised carbolic acid and concentrated sulphuric acid. This is heated to 100° until a sample is found to be completely soluble in water, when a double equivalent of nitric acid of 1·3 sp. gr. is allowed to flow in, the whole being continually agitated. In some works, the phenol-sulphonic acid, slightly diluted, is run into strong nitric acid. On cooling, the product forms a crystalline mass, which is filtered off, drained, and washed with cold water. It is then purified by crystallisation from boiling water containing 0·1 per cent. of sulphuric acid; or the hot solution of the crude acid is exactly neutralised with sodium carbonate, the liquid filtered to separate resin, and excess of sodium carbonate added to the filtrate, when almost the whole of the sodium picrate separates. This salt is decomposed by sulphuric or hydrochloric acid and the picric acid crystallised. Sodium sulphate is sometimes added before crystallisation, as an adulterant.

[2] The first product of the action of nitric acid on phenol is a mixture of para-mononitrophenol, $C_6H_4(NO_2).OH$, with the isomeric ortho-derivative. These bodies are best obtained by adding sufficient water to pure phenol to prevent it from solidifying on cooling, and then adding the resultant hydrous phenol drop by drop to a well-cooled mixture of two parts of nitric acid of 1·34 sp. gr. and four parts of water. A heavy bromine-like oil separates, and on prolonged standing sets to a crystalline mass. This consists of a mixture of ortho- and para-nitrophenol, with some unaltered phenol. The higher the temperature has been allowed to rise the larger the proportion of the ortho-modification formed. The product is washed with cold water, and then distilled in a current of steam, when the ortho-nitrophenol dissolves over, and may thus be separated from the para-modification,

Picric acid forms pale yellow, crystalline needles or scales, of an intensely bitter taste and 1·777 specific gravity. The pure acid melts at 122° C. and the common at a lower temperature to a brownish-yellow oil, which at a higher temperature partially sublimes, and boils with formation of yellow, bitter, suffocating vapours. The lower melting point of impure picric acid is probably due to an admixture of dinitrophenols or of a nitrocresol. Hence the melting point of picric acid is a test of its purity.

When strongly heated, picric acid burns rapidly with formation of an intensely black smoke. It is commonly stated to be liable to explode when strongly heated, but this is doubtful, and is opposed to the direct experiments of Dupré and Abel. On the other hand, picric acid can be detonated by a blow, a charge

which is not volatile, and may be obtained from the contents of the distilling flask by cooling and recrystallising from boiling water.

A meta-mononitrophenol is obtainable from meta-nitraniline by the action of nitrous acid.

On warming the ortho-mononitrophenol with nitric acid of 1·36 sp. gr., violent action ensues and another nitro-group is assimilated, a product being obtained which is chiefly a mixture of diortho-dinitrophenol and ortho-para-dinitrophenol, $C_6H_3(NO_2)_2.OH$. (The latter body is also obtained by the further nitration of para-mononitrophenol.) The product is washed with cold water, and then boiled with water in a flask through which a current of steam is passed, to remove unaltered mono-nitrophenol. It is then boiled with water and excess of barium carbonate, and the solution filtered. On cooling to 40°, the barium salt of diortho-dinitrophenol crystallises out, while the corresponding salts of ortho-para-dinitrophenol and picric acid remain in solution. A better separation of the barium salts of the isomeric dinitrophenols can be obtained by rectified spirit, in which the ortho-para-salt dissolves with moderate ease, while the diortho-compound is nearly insoluble. Salkowski converts the mixed barium salts into potassium salts by potassium carbonate, and removes the greater part of the ortho-para-salt by crystallisation; then heats the mother-liquor to 40°–50° C. and precipitates with barium chloride, which throws down the diortho-compound. This is washed with cold water and purified by recrystallisation. From their salts the dinitrophenols may be obtained free by adding excess of dilute sulphuric acid and agitating with ether. The ethereal layer leaves the nitrophenol on evaporation.

A meta-mononitrophenol is obtainable by indirect means, and yields on treatment with nitric acid three isomeric di- and two tri- nitrophenols which are not identical with those produced by the direct action of nitric acid on phenol. By the action of boiling concentrated nitric acid the meta-dinitrophenols are converted into trinitroresorcinol or styphnic acid, $C_6H(NO_2)_3.(OH)_2$.

of 5 grains of fulminate of mercury sufficing to determine the explosion. The detonation of one charge will cause the detonation of neighbouring quantities, and even wet picric acid can be exploded by this means. Metallic picrates, and notably picrate of lead, or even an imperfect mixture of picric acid with oxide or nitrate of lead, will detonate violently when heated, and the explosion will induce the detonation of neighbouring quantities of picric acid or picrates.[1] This property of the picrates has led to their employment in several detonating and explosive mixtures (see page 143).

The following table summarises the properties of the nitrophenols at present known :—

Formula.	Name.	Position of the NO_2 group, OH being 1.	Melting point ° C.	Characters.
$C_6H_4(NO_2).OH$.	Para-mononitrophenol.	4	114	White prisms; not volatile in a current of steam.
Do.	Meta-mononitrophenol.	3	96	Almost colourless prisms or feathery plates; not volatile with steam.
Do.	Ortho-mononitrophenol.	2	45	Pale yellow prisms; readily volatile with steam.
$C_6H_3(NO_2)_2.OH$.	α–or Para-ortho-dinitrophenol.	2 : 4	114	Striated, yellowish-white plates united in fern-like forms.
Do.	β–or Diortho-dinitrophenol.	2 : 6	64	Slender, short, bright yellow needles.
Do.	γ–Dinitrophenol.	3 : 6	104	Slender, short, pale yellow needles; volatile with steam.
Do.	δ–Dinitrophenol.	3 : 4	134	Long, colourless, silky needles; not volatile with steam.
Do.	ε–Dinitrophenol.	2 : 3	144	Small yellow needles.
$C_6H_2(NO_2)_3.OH$.	α–or Para-diortho-trinitrophenol (picric acid).	2 : 4 : 6	122	Pale yellow laminæ or prisms; not volatile with steam.
Do.	β–Trinitrophenol (from meta-nitrophenol).	3 : 4 : 6	96	White satiny needles or scales.
Do.	γ–Trinitrophenol.	2 : 3 : 6	117	White needles.

---

[1] At midday on June 22, 1887, a fire, followed by a violent explosion, occurred at the works of Messrs Roberts, Dale, & Company, Cornbrook, Manchester, manufacturers of picric acid. One man was killed, the works were completely destroyed, and much damage was done to the neighbouring buildings. The verdict of the coroner's jury was based on the evidence of Colonel Majendie, chief inspector of explosives, and was to the effect that the fire was caused by forbidden smoking, and that the fire ignited picric acid and litharge or other oxidising agent which had been accidentally mixed and fused owing to the negligent manner in which they were stored, and so caused the explosion.

Picric acid is soluble in about 15 parts of boiling water, but it requires 26 parts at 76° and 86 at 15° C. The solution is intensely bitter, bright yellow, and reddens litmus. In a stratum one inch in depth, the yellow colour of a solution of 1 part of picric acid in 30,000 of water is distinctly visible. The yellow colour of picric acid solutions is intensified by neutralisation with an alkali.

Picric acid is readily soluble in alcohol, ether, chloroform, benzene, petroleum spirit, &c.; the last four solutions being colourless or nearly so. Such of the above solvents as are not miscible with water remove picric acid more or less perfectly from its aqueous solution, or that of a picrate which has been freely acidulated with sulphuric acid. Ether is preferable to chloroform for this purpose.

All the above solutions of picric acid, including the aqueous, dye silk, wool, skin, and other nitrogenous organic matters a yellow colour of a slightly greenish shade.[1] The stain is not removable by water, but soap or alkali partly destroys it. Animal charcoal absorbs a large quantity of picric acid from its aqueous solution.

Picric acid forms a series of well-defined crystallisable metallic salts and also combines with organic bases. With certain hydrocarbons it forms characteristic crystalline compounds of the formula X, $C_6H_3(NO_2)_3O$, in which X represents a molecule of the hydrocarbon. The reaction has been utilised for the purpose of distinguishing hydrocarbons, especially those of the anthracene group (see vol. ii. page 524), and the formation of the naphthalene and acridine picrates has been suggested as a means of identifying picric acid.

DETECTION AND DETERMINATION OF PICRIC ACID.—The yellow colour and extremely bitter taste of the aqueous solution of picric acid, the deepening of the yellow colour on adding excess of alkali, and the power possessed by the solution of the free acid of dyeing immersed wool or silk yellow, are themselves important indications of its presence. In the presence of other colouring or interfering bodies, the picric acid may be extracted from the aqueous solution by agitation with ether or amylic alcohol, after strongly acidulating with sulphuric acid. The picric acid may then be recovered by evaporating the ethereal solution, or agitating it with solution of caustic soda, when it will pass into the alkaline liquid. The extraction of picric acid from an acidulated solution by ether, benzene, or amylic alcohol may be made quantitative.

---

[1] Picric acid is used as a dye for silk and wool, but is employed to modify the shades of other colours rather than as an unmixed dye. Thus with methyl-green it gives a yellow-green, with indigo-carmine or aniline-blue a deep green, and with magenta a very fast scarlet. Since the introduction of the yellow azo-dyes the employment of picric acid has decreased.

Picric acid may be titrated with ease and accuracy by standard caustic alkali and phenol-phthaleïn (P. Kay, *Jour. Soc. Dyers, &c.*, iv. 84). The process is applicable to the ethereal or benzene solution of picric acid if this be first diluted with alcohol.

An aqueous solution of picric acid is not precipitated on adding neutral lead acetate, but basic or ammoniacal lead acetate gives a bright yellow precipitate even with very dilute solutions of picric acid.[1]

Picric acid is not precipitated from its aqueous solution by cupric sulphate; but the ammonio-sulphate produces a bright green precipitate, which is insoluble in ammonia, and is decomposed by washing with water. A solution containing 1–10,000 of picric acid gives a distinct precipitate with ammonio-sulphate of copper in twenty-four hours.

If a solution of picric acid be treated with zinc and dilute sulphuric acid, a turbid yellowish-red solution is obtained, which, when poured off from the excess of zinc and mixed with alcohol, develops a green colour, changing through blue to a violet.

By the action of tin and hydrochloric acid in a warm solution, picric acid is completely reduced to the colourless hydrochloride of triamido-phenol, $C_6H_2(NH_2)_3.OH$. In alkaline solutions, the reduction does not proceed so far, picramic acid, $C_6H_2(NO_2)_2(NH_2).OH$, being the product. This reaction occurs most readily by passing sulphuretted hydrogen through a saturated alcoholic solution of picric acid neutralised with ammonia. Dark red crystals of ammonium picramate are deposited, from which the free acid may be prepared by dissolving in hot water and adding acetic acid. Picramic acid forms beautiful red needles, almost insoluble in water even when hot, but soluble in alcohol and ether. It dyes silk and wool brown.[2]

---

[1] If the precipitate be decomposed by dilute sulphuric acid, and the filtered solution rendered ammoniacal and evaporated to dryness, a residue is obtained which gives a deep brown colour on heating with potassium cyanide. This behaviour distinguishes picric acid from quercitron and such other vegetable yellow colouring matters as are precipitated by basic lead acetate.

[2] E. Turpin has patented (No. 10,665, 1887) the use, as a substitute for gunpowder, of the product resulting from the reduction of picric acid by boiling its aqueous solution with metallic zinc or iron. When acetic acid is also added picramic acid is formed, and this, or its sodium salt, in admixture with nitre, yields a powerful detonating explosive. Mixtures containing from 30 to 50 per cent. of picramic acid, or 25 to 53 of sodium picramate, are recommended.

The nature of the French explosive *mélinite* has not been made public, When a solution of picric acid is boiled with a strong solution of potassium cyanide, a deep red liquid is produced,[1] owing to the formation of potassium iso-purpurate, a body which crystallises in small reddish-brown plates with a beetle-green lustre, and is slightly soluble in cold but more readily in hot water. By reaction with ammonium chloride, it gives ammonium iso-purpurate, $NH_4,C_8H_4N_5O_6$, or artificial *murexide*, which in a slightly acid bath dyes silk and wool a beautiful brown-red colour. It was formerly employed under the name of "grenat soluble," but is not now used. On adding barium chloride to a solution of either of the above salts a vermilion-red precipitate is formed, consisting of barium iso-purpurate. True iso-purpuric acid is very unstable and is practically unknown.

Picric acid, when boiled with a strong solution of calcium hypochlorite (bleaching powder), gives off pungent and tear-exciting vapours of chloropicrin, $C(NO_2)Cl_3$.

Picric acid forms highly insoluble compounds with many of the vegetable alkaloids,[2] and the insolubility of the cinchonine salt has been employed for the determination of picric acid. A solution of cinchonine sulphate acidulated with sulphuric acid is added to the picric acid solution. The precipitate of picrate of cinchonine, $C_{20}H_{24}N_2O(C_6H_3N_3O_7)_2$, is washed with cold water, rinsed off the filter into a porcelain crucible or dish, the water evaporated on the water-bath, and the residual salt weighed. The yellow, intensely bitter alkaloid, berberine, is said to precipitate picric acid so perfectly that, on mixing the picric and alkaloidal solutions in equivalent proportions and filtering, the filtrate is colourless and perfectly free from bitter taste.

Some of the colour-bases from coal-tar form extremely insoluble picrates, and have been employed by Kay and Appleyard (*Jour. Soc. Dyers, &c.*, iv. 83) for the determination of picric acid.

---

but its composition is not improbably indicated by that of the foregoing mixtures; or perhaps has a connection with another patent of the same inventor (No. 10,667, 1887), who has proposed the use, as explosives, of chloro-picrin, bromo- chloro- and iodo-dinitrophenols, bromo-dinitrobenzene, chloro-trinitrobenzene, and tetranitro-chloronaphthalene.

[1] Aniline yellow of commerce dissolves in water with redder colour than picric acid. It is not altered by potassium cyanide, but is turned purple by hydrochloric acid.

[2] The cinchona alkaloids, the opium bases (except morphine and pseudo-morphine), the *strychnos* alkaloids, veratrine, berberine, and some others are completely precipitated by picric acid from their dilute solutions, if acidulated by sulphuric acid, but not in presence of free hydrochloric acid. Caffeine and the glucosides are not precipitated by picric acid.

For this purpose they prefer the dye known as night-blue, which is the hydrochloride of tetramethyltolyltriamido-diphenyl-naphthyl-carbinol. The commercial product is purified by precipitating the aqueous solution with ammonia, washing well with water, and drying the precipitate over strong sulphuric acid. A weighed quantity of the base is dissolved in acetic acid and the solution diluted to a known volume. For the titration, a known volume of the night-blue solution is measured into a flask, and the solution of picric acid run in from a burette. 485 parts of the night-blue base correspond to 229 of picric acid, the picrate, which forms a dark precipitate, having the formula $C_{34}H_{36}N_3.C_6H_2(NO_2)_3OH$. The picric acid solution should contain 1 gramme of the sample per litre, and by comparing the volume of the solution used with the measure of a solution of pure picric acid employed in a parallel experiment, the proportion of impurity may be readily ascertained. The end of the reaction is very sharply defined, as by tilting the flask on one side, so that a portion of the clear liquid may run into the neck, it is easy to observe whether the solution retains any blue colour. A very slight excess of picric acid is sufficient to produce a marked yellow tint. If desired, a portion of the liquid may be filtered for the better observation of its colour, but this is rarely necessary.

Crystal violet, the hydrochloride of hexamethylrosaniline, may be substituted for the night-blue in the above process. 443·5 parts of this colouring matter, when dissolved in water, react with 229 parts of pure picric acid to form a picrate of the formula $C_{25}H_{31}N_3.C_6H_2(NO_2)_3OH$. This precipitate is flocculent, and when in suspension exhibits such a powerful coppery reflex that the liquid containing it appears brown by reflected light.

The picrates of rosaniline, safranine, methyl-violet, and malachite-green are also nearly insoluble in water, but not sufficiently so to render the bases desirable substitutes for night-blue or crystal-violet in the above process.

Of the compounds of picric acid with solid hydrocarbons, that with naphthalene, $C_{10}H_8+C_6H_3(NO_2)_3O$, is almost the only one precipitated when the cold alcoholic solution of the hydrocarbon is mixed with a cold alcoholic solution of picric acid. It forms stellate groups of golden-yellow needles, melting at 149° C. The formation of naphthalene picrate may be employed to distinguish picric acid from similar nitro-compounds.

Acridine has been suggested by Anschütz (*Jour. Soc. Chem. Ind.*, iii. 234) as a suitable reagent for the determination of picric acid, the hydrochloride being used as a precipitant for metallic picrates and a solution of the free base in benzene for the picric acid compounds of hydrocarbons.

Picric acid has been used occasionally to communicate a bitter taste to *beer*, less than 1 grain per gallon being amply sufficient for this purpose. The employment of picric acid as a "hop-substitute" is objectionable, as it has distinct poisonous properties, and rabbits and dogs have been killed by doses varying from 0·06 to 0·60 gramme. The most delicate or satisfactory method for the detection of picric acid in beer is to concentrate 100 c.c. by evaporation to about 30 c.c.; then acidulate with sulphuric acid and agitate with ether or petroleum spirit. The ethereal solution is separated and evaporated. The residue is dissolved in hot water and the solution heated on the water-bath for some time with a small quantity of white Berlin wool, which in presence of picric acid will acquire a yellow colour. The author has readily detected 1 part of picric acid in 100,000 of beer by this method. Amylic alcohol has been proposed as a substitute for ether, but, in the opinion of the author, is not so satisfactory. By first precipitating the beer with neutral acetate of lead and filtering, the colouring matter of the beer may be removed and the indications made more delicate. As a confirmation, the dye may be removed from the wool by warming it with dilute ammonia, filtering, and evaporating the filtrate to a very small bulk on the water-bath. On then adding a few drops of potassium cyanide solution, and heating, a distinct red-brown colour will be produced in presence of picric acid;[1] or the ammoniacal extract may be treated with zinc and hydrochloric acid and the solution diluted with alcohol, as described on page 143.

It is evident that the method just described is applicable to the detection of picric acid on animal fibres, such as *silk* or *wool*.

COMMERCIAL PICRIC ACID.

The picric acid of commerce is generally crystallised. Though now of much better quality than formerly, it is still liable to contain impurities, and occasionally is intentionally adulterated. Thus sodium sulphate is sometimes added before crystallisation, and oxalic acid and sugar are said to be occasionally met with.

The melting point of pure picric acid is 122° C., and the best commercial samples do not melt below 121°. A lower melting point indicates the presence of *dinitrophenol* or a *nitrocresol*. The first impurity is due to imperfect nitrofication and the latter to the employment of a carbolic acid of low melting point (therefore containing cresol) for the manufacture. The melting point of picric acid is best observed by placing a minute fragment of the sample on the surface of some clean mercury contained in a porcelain crucible or small beaker. The latter is covered with an inverted funnel or bottomless flask, through the neck of which a thermometer passes and is held by a perforated cork in such a position that the bulb may be entirely immersed in the mercury, without touching the side or bottom of the beaker or crucible. The latter is now heated on an iron plate, and the temperature at which the fragment of picric acid liquefies recorded as the melting point. By employing several fragments and repeating the experiment after allowing the mercury to cool a few degrees, very fairly concordant results are obtainable.

---

[1] A rough colorimetric determination of the amount of picric acid present may be based on the depth of colour produced.

More rapid, and for technical purposes quite as satisfactory, results are obtainable by determining the solidifying point of the sample. This is effected by melting 8 or 10 grammes of the picric acid in a small test-tube, which is then fixed by means of a perforated cork in the mouth of an empty, short-necked flask. The melted picric acid is continually stirred with a thermometer, while the temperature is carefully watched. At a certain point the mercury ceases to fall, remaining stationary for fully half a minute, or even rising again slightly. This temperature, which is perfectly definite, is recorded as the solidifying point of the sample.

The following figures, obtained in the author's laboratory by the examination of six samples of commercial picric acid, show the constancy of the results yielded. It will be observed that, while the solidifying point is always several degrees lower than the melting point of the same sample, the difference between the two results is not a constant figure :—

Sample.	Melting Point °C.	Solidifying Point °C.	
		Observations.	Mean.
A	122, 122	115, 115, 115·5, 115, 115.	115·1
B	118, 188	114, 118, 112, 113, 113·5, 113, 118.	113·1
C	121, 121	115·5, 116, 115.	115·5
D	120, 119	114·5, 114·5.	114·5
E	117·5, 117·5	113·5, 112·5.	113·0
F	122, 122	117, 117, 118, 118, 118, 117, 118, 118, 118.	117·7

Picric acid of good quality does not melt when boiled with twice its weight of water. If fusion occur, it is probably due to the presence of nitrocresols, which for some purposes are objectionable.

The best commercial picric acid is completely soluble in 15 times its weight of boiling water, or leaves only a trifling quantity

(0·5 per cent.) of *granular* impurity. Picric acid of inferior quality leaves a *melted globule* when similarly treated. The scientific advisers of the French Government call this insoluble matter "dinitrophenol" (!), apparently without any evidence of its nature, and reject, as unsuited for the manufacture of mélinite,[1] all picric acid which leaves a globule amounting to more than 1 per cent. of the sample. The test is made by treating 10 grammes of the acid with 150 c.c. of water, and heating the liquid to boiling in a flask with gentle agitation, till the globule of insoluble matter becomes transparent and ceases to diminish perceptibly in bulk. This point is reached in about ten minutes from the commencement of ebullition. The test must not be much prolonged, or the so-called "insoluble matter" will partly dissolve. The critical point is by no means well defined, though with care and experience fairly concordant results are obtainable with some samples, while others behave very erratically. When the operation is considered to be complete, the liquid is allowed to cool slightly and poured off from the globule of "dinitrophenol," which is then washed with cold water, dried by means of filter-paper, and weighed.

Any *resinous matters* will also be left insoluble on dissolving commercial picric acid in boiling water. The separation will be more perfect if the hot solution be exactly neutralised with caustic soda.

Besides being soluble in 15 parts of boiling water, picric acid of good quality dissolves completely in 10 parts of alcohol, while any metallic *sulphates* or *nitrates* will be left insoluble.

General impurities and adulterations may be detected and determined by treating 2 grammes of the finely-powdered sample with 50 c.c. of ether. The picric acid dissolves, while any picrates, nitrates, oxalic acid, boric acid, sodium sulphate, alum, sugar, &c., will be left insoluble, and, after removal of the ethereal liquid, may be readily identified and determined. For the detection and determination of *water* and *oxalic acid*, 50 c.c. of warm benzene may be advantageously substituted for the ether. Sugar and boric acid may be separated from the other impurities by treating the residue insoluble in ether or benzene with rectified spirit. If *boric acid* be present the alcoholic solution will burn with a green flame. *Sugar* may also be sought for by neutralising the aqueous solution of the sample by sodium carbonate, evaporating to dryness, and extracting with proof-spirit, which will dissolve any sugar and leave the sodium picrate insoluble.

Sulphuric, hydrochloric, and oxalic acids, and their salts, may be detected by adding solutions of barium, silver, and calcium, respectively, to the warm, filtered, aqueous solution of the sample. 0·2 per cent. of SO_3, as estimated by precipitation as barium sulphate, is the maximum proportion allowed by the French Government in picric acid intended for the manufacture of mélinite. *Free sulphuric acid* might be detected by dissolving the sample in warm benzene, agitating the solution with warm water, removing the benzene layer, and again agitating the aqueous liquid with benzene, till all yellow colour is removed. On then titrating the aqueous liquid with standard alkali, the volume required for neutralisation will correspond to the free sulphuric or other mineral acid of the sample.

---

[1] See footnote on page 143.

It is possible that commercial picric acid occasionally contains a *nitrophenol-sulphonic acid.* Such an impurity would be indicated by the presence of sulphates in the residue obtained on igniting the sample after neutralisation with a fixed alkali. The explosive character of the picrates prevents the direct application of this method, but ignition of the picric acid in admixture with a large excess of lime or magnesia would probably answer, or the sample might be dissolved in alcohol together with some ammonium carbonate, and the alcohol burnt in a lamp connected with an apparatus similar to that employed for determining the proportion of sulphur in coal-gas. (See *Analyst*, xiii. 43.)

If the process of nitrofication has been imperfect, the resultant picric acid will be liable to contain *dinitrophenol* (see above). This impurity lowers the melting point of the sample. The calcium salt is less soluble than calcium picrate, and if present in sufficient quantity may be separated from the latter by fractional crystallisation, or by precipitating the hot saturated aqueous solution of the sample with excess of lime-water.

The most promising, if not the only method of determining small proportions of dinitrophenol in picric acid is by treating the aqueous solution of the sample with bromine, as proposed by the author (*Jour. Soc. Dyers, &c.*, iv. 84). With dinitrophenol the following reaction occurs:—$C_6H_3(NO_2)_2OH + Br_2 = HBr + C_6H_2Br(NO_2)_2OH$. With picric acid, bromine reacts as follows:—$C_6H_2(NO_2)_3OH + Br_2 = HBr + HNO_3 + C_6H_2Br(NO_2)_2OH$.[1] In each case two atoms of bromine enter into the reaction, with formation of a bromo-dinitrophenol (the same in each case) and one molecule of hydrobromic acid. But in the case of picric acid nitric acid is formed in addition, and hence the acidity of the liquid at the end of the reaction would be greater the larger the proportion of picric acid present. If the bromo-dinitrophenol and excess of bromine[1] were removed by agitation with ether or similar solvent, the acidity of the aqueous liquid could be ascertained with great accuracy by titration with standard alkali.

---

[1] See footnote on page 143, referring to bromo-dinitrophenol as an explosive.

The author found the reaction between bromine and dinitrophenol to occur instantaneously, but in the case of picric acid it was gradual. In twelve hours it was complete, but in the course of a few minutes almost nothing. This fact enables the reaction with bromine to be utilised for the direct determination of the dinitrophenol, instead of for its indirect estimation (by determining the picric acid), as when the acidity is ascertained. The following method of operating was found by the author to be the most satisfactory:—1 gramme of the sample of picric acid is dissolved in about 100 c.c. of warm water. A saturated solution of bromine in water is diluted with twice its measure of water in a large tapped and stoppered separator, and from this run into a Mohr's burette. From this burette, a definite volume of the bromine solution, which is approximately of 1 per cent. strength, is run into a flask and an equal measure into another similar flask, both of which are immediately closed. The picric acid solution is then poured into one of the flasks, the last drops rinsed in without delay, and then an excess of a solution of potassium iodide at once added to the contents of both flasks. The liberated iodine is then determined by titration with a decinormal solution of sodium thiosulphate (hyposulphite) in the usual way.[2] From the difference in the volume of the solution required in the two experiments the amount of bromine which has reacted with the dinitrophenol is easily found. *Dinitrophenol* reacts with 86·96 per cent. of bromine, taking up 43·48 per cent. *Mononitrophenol*, if present, which is improbable, would react with 230·2 per cent. of bromine, taking up 115·1 per cent. to form the compound $C_6H_2Br_2(NO_2).OH$. The author has verified these reactions by experiments on specially prepared mono- and dinitrophenol. When the process is applied to commercial picric acid the results are liable to be somewhat in excess of the truth, owing to slight action of the bromine on the picric acid itself.

Commercial picric acid often contains particles of a red colour. These are often attributed to the presence of dinitrophenol, but from an observation of T. Whitaker (*Jour. Soc. Dyers, &c.,* iv. 87) it is not improbable that they consist of a *nitrosophenol.*

---

[1] If preferred, before extracting with ether the excess of bromine may be got rid of by adding potassium iodide and then sufficient sodium thiosulphate to react with the iodine liberated.

[2] The author found iodine to be wholly without action on solutions of either mono-, di-, or tri-nitrophenol.

METALLIC PICRATES.

As a rule, the picrates are possessed of but little solubility. They are yellow in colour, and crystallise well. Many of them explode violently when heated or struck, and hence they are employed in admixture with metallic chlorates or nitrates for the blasting charge of shells. (See footnote on page 143.)

Potassium picrate, $C_6H_2(NO_2)_3.OK$, forms long yellow needles when a strong solution of picric acid is neutralised by carbonate or hydroxide of potassium. The salt requires 288 of cold or 14 parts of boiling water for solution, and in alcohol is nearly insoluble. The aqueous solution is much more strongly coloured than a solution of free picric acid of corresponding strength. When heated, potassium picrate becomes red and explodes like gunpowder, and when strongly struck it detonates violently.

Sodium picrate is readily soluble in pure water, but nearly insoluble in solution of carbonate of sodium.

Ammonium picrate crystallises in rhombic scales which are somewhat more soluble than the potassium salt. It has been suggested for use as an antipyretic.

Lead picrate crystallises in brown needles soluble in 119 parts of cold water. In admixture with nitre it is employed as an explosive. A rough mixture of picric acid with red lead or litharge detonates violently when strongly struck.

Nitrophenol-sulphonic Acids.

The mono- and dinitro-derivatives of phenol are, like phenol itself, acted on by strong sulphuric acid with formation of sulphonic acids. If a mono-nitrophenol be sulphonated, the product can be converted into a dinitrophenol-sulphonic acid by careful nitrofication, but if the treatment with nitric acid be pushed to an extreme the product is invariably picric acid, the sulphonic group being eliminated.

The sulphonated nitrophenols furnish two classes of salts:—*normal salts* in which only the hydrogen of the sulpho-group is replaced by metals, and *basic salts* in which the hydrogen of the hydroxyl group is also replaced. The former salts are yellow, but the latter are red, and often of great beauty.

FLAVAURIN. The commercial colouring matter known under this name is the ammonium salt of dinitrophenol-parasulphonic acid, $C_6H_2(SO_3NH_4)(NO_2)_2.O(NH_4)$. It is produced by the cautious action of nitric acid on mononitrophenolparasulphonic acid, and the conversion of the product into an ammonium salt. Flavaurin forms a yellowish-red powder which swells up like a "Pharaoh's serpent" when heated. The aqueous solution is yellow, and is changed to wine-red by hydrochloric acid. With caustic soda the solution is darkened, and ammonia is evolved on heating. On boiling the alkaline liquid with zinc dust it turns brown, and is then decolorised, air restoring the brown colour. Flavaurin dissolves in strong sulphuric acid with wine-red colour, the solution becoming colourless on dilution.

Nitrocresols.

When the mixture of isomeric cresols, $C_6H_4(CH_3).OH$, from coal-tar, forming the fraction of the phenolic bodies boiling at about 200° C., is treated with nitric acid, the orthocresol and paracresol are converted respectively into dinitro-orthocresol and dinitro-paracresol, respectively. The metacresol, which is the most abundant of the isomeric cresols, is, on the other hand, converted into trinitro-metacresol, melting at 160°. The isomeric dinitrocresols can be separated by taking advantage of the difference in the solubility of their barium salts. They may also be obtained by acting on the corresponding toluidines in ice-cold hydrochloric acid solution with sodium nitrite, when diazotoluene chloride, $C_6H_4(CH_3)N:NCl$, is formed, and if this be poured into hot nitric acid the dinitrocresol is formed, and crystallises out on cooling.

DINITROCRESOLS, $C_6H_2(CH_3)(NO_2)_2.OH$, in their physical and general properties closely resemble picric acid, but are volatile and more readily explosive. The salts of dinitro-orthocresol are generally yellow; but those of the para-compound are usually red, and soluble in water with more or less orange colour.

VICTORIA YELLOW is a mixture of the sodium salts of dinitro-ortho- and dinitro-para-cresol, $C_6H_2(CH_3)(NO_2)_2.ONa$.

GOLD YELLOW is the corresponding potassium salt, and closely resembles victoria yellow.

The dinitrocresylates form soluble reddish-yellow powders which dissolve in strong sulphuric acid with pale yellow colour. They are violently explosive in a dry state. The dinitrocresylates closely resemble the picrates, but on adding hydrochloric acid to the cold aqueous solution the liquid is decolorised; or if sufficiently concentrated, yields a precipitate of free dinitrocresol in pale yellow needles, and the liquid obtained on filtering in the cold is colourless, whereas that yielded by a picrate has a marked yellow colour. Similarly, hydrochloric acid decolorises a tissue dyed with a dinitrocresylate, the yellow colour being restored by washing. Warm water removes victoria yellow from the fibre, and the solution is decolorised by hydrochloric acid as described above.

Solutions of victoria yellow are unchanged by caustic soda and ammonia, but on boiling with potassium cyanide yield a brown-red liquid similar to that produced with picric acid.

According to H. Fleck, dinitrocresol and its salts can be distinguished from picric acid by warming the concentrated solution for a few minutes with hydrochloric acid, and then adding a fragment of metallic zinc. After standing in the cold from half an hour to two hours, the liquid will become a beautiful blue if picric acid be present, or a bright blood-red with dinitrocresol. Mere traces of these colouring matters are said to be recognisable by the test. In examining farinaceous foods for dinitrocresol, &c., the substance should be exhausted with alcohol, and the test applied to the residue obtained.

The salts of dinitrocresol are very irritating as well as fugitive, and hence are not now used as dyes.

The salts of dinitrocresol have been employed, under the name of "saffron-surrogate," for colouring butter, cheese, macaroni, &c. For this purpose they are very ill-suited, as they have distinct poisonous properties. T. Weyl (*Ber.*, xx. 2835; xxi. 212) found that doses of 0·054 gramme for every kilogramme in weight of the animal experimented upon, suspended in milk or water and poured directly into the stomach, in the case of dogs produced vomiting followed by difficulty of breathing, and finally severe cramp in the extremities, the majority of cases terminating fatally. Administered to rabbits, in doses of 0·54 gramme per kilogramme, dinitrocresol caused convulsions, paralysis of the pupil, and great difficulty in breathing, death ensuing from suffocation in twenty to thirty minutes.

Nitronaphthols.

The two modifications of naphthol, $C_{10}H_7.OH$, yield on nitrofication bodies analogous to those obtained by similar means from phenol and cresol. The dinitro-derivative of alpha-naphthol is the most important.

DINITROALPHANAPHTHOL, $C_{10}H_5(NO_2)_2.OH$, is obtained from α-naphthylamine, α-$C_{10}H_7.NH_2$, by converting it into the diazo-chloride, which on treatment with nitric acid yields the corresponding dinitronaphthol. It may also be obtained by dissolving α-naphthol in concentrated sulphuric acid, diluting the resulting sulphonic acid with water, adding nitric acid, and heating gently, when the dinitro-derivative is deposited in minute yellow needles. The product may be purified by converting it into its calcium or ammonium salt, which after recrystallisation is decomposed by an acid.

Dinitronaphthol forms yellow needles, melting at 138° C., and somewhat readily volatile. It is nearly insoluble in water, but soluble in alcohol and ether. It closely resembles picric acid, and forms a series of beautiful and well-crystallised *salts* yielding golden yellow solutions, which are decolorised by hydrochloric acid, a yellowish-white precipitate of the free acid being produced, soluble in ether. Ammonia is without action. Caustic potash and soda produce orange-red precipitates in strong solutions. Potassium cyanide and ammonium sulphide react as with picric acid.

The *sodium salt* of dinitronaphthol forms readily soluble glittering needles containing $C_{10}H_5(NO_2)_2ONa + H_2O$, and deflagrates when heated. The *ammonium salt* burns off quietly when heated, and is soluble in alcohol. The *calcium salt* forms yellowish-red crystals of the formula $[C_{10}H_5(NO_2)_2O]_2Ca + 6H_2O$.

The potassium, sodium, ammonium, and calcium salts of dinitronaphthol have been extensively employed as colouring matters under the names of

NAPHTHALENE YELLOW; NAPHTHOL YELLOW; MANCHESTER YELLOW; Martius' Yellow; Gold Yellow. In an acid bath this body dyes silk and wool (but not cotton) a brilliant yellow colour, free from the greenish reflection peculiar to fabrics dyed with picric acid. Owing to the volatility of dinitronaphthol (which is liberated by the acid of the bath), the colour marks and rubs off, and hence the employment of naphthalene yellow as a dye has much diminished.

Naphthol yellow is very commonly adulterated with *dextrin* and *sodium sulphate*, the proportion of the latter admixture sometimes reaching 50 per cent. It is sometimes adulterated with *picric acid*, to detect which a sample should be dissolved in water, the cold solution acidulated freely with hydrochloric acid, and the liquid filtered. If picric acid be present the filtrate will have a marked yellow colour, and the acid can be obtained in crystals by evaporation.

Naphthalene yellow may be distinguished from picric acid by boiling wool in the acidified solution, washing it, heating it with ammonio-sulphate of copper, and again washing. When a fibre or fabric dyed with picric acid is boiled with the alkaline copper solution it turns bluish-green, but if naphthalene yellow has been used an olive-green tint results.

When a material dyed with naphthol yellow is wrapped in white paper and heated to 120° C. in an air-bath, part of the yellow colour is transferred to the paper. Hot water or hot dilute ammonia dissolves out the colouring matter, and the yellow solution is decolorised by hydrochloric acid, a yellow-white precipitate being produced (distinction from picric acid).

Naphthalene yellow is sometimes employed for colouring butter, cheese, macaroni, mustard, saffron, &c., for which applications its marked poisonous characters render it very unfit[1] (see page 153). The detection of butter-colorants will be described under "Annatto."

HELIOCHRYSIN, or *Sun gold*, is the commercial name of an unstable colouring matter consisting of the sodium salt of tetranitronaphthol, $C_{10}H_3(NO_2)_4.ONa$.

Nitronaphthol-sulphonic Acids.

When alphanaphthol is warmed with excess of fuming sulphuric acid it yields a trisulphonic acid, which on subsequent treatment with strong nitric acid yields, on cooling, crystals of

DINITROALPHANAPHTHOL-SULPHONIC ACID, $C_{10}H_4(SO_3H)(NO_2)_2OH$. The product is purified by recrystallisation. It forms long yellow needles, readily soluble in warm water, but insoluble in ether. These characters distinguish it from picric acid, dinitro-naphthol, &c. Its salts are easily crystallisable, said to be non-poisonous,[1] and dye wool and silk (but not cotton) a bright yellow colour, which is fast in the light, non-volatile, and does not mark or rub off. For these reasons the salts have largely replaced picric acid and the dinitro-naphtholates.

Potassium Dinitro-α-naphthol-sulphonate, $C_{10}H_4(SO_3K)(NO_2)_2.OK$, forms an orange-yellow precipitate on mixing a strong solution of the free acid with one of potassium sulphate. It is sparingly soluble in cold, but readily in hot water. By boiling it with strong hydrochloric acid the free acid, or, according to some, an *acid salt*, $C_{10}H_4(SO_3K)(NO_2)_2OH$, is formed.

The sodium and ammonium salts of dinitronaphthol-sulphonic acid are freely soluble, but the *barium* and *lead* salts only sparingly so.

The *salts* of dinitronaphthol-sulphonic acid are yellow or orange.

---

[1] Comparatively small doses of naphthalene yellow are said to cause asthmatic breathing, a considerable rise of temperature (without convulsions), and ultimately death (*Comp. rend.*, 1885, p. 101). According to Weyl (*Ber.*, xxi. 2191), Martius' yellow is well tolerated by rabbits, but small doses proved fatal to dogs. A dog weighing 6850 grammes, to which a dose of 0·5 gramme of dinitronaphthol was given on two successive days, and 1 gramme of the sodium salt on the third day, died on the fourth day. Less than 1 gramme given subcutaneously caused the death of a similar dog. On the other hand, naphthol yellow S proved innocuous to dogs in four times these amounts.

On heating, they swell up and emit sparks, but do not deflagrate. The solutions are yellow or brownish-yellow, becoming pale yellow on adding hydrochloric acid, but no precipitate is produced, and the diluted acid liquid is not decolorised by agitation with ether. (Distinction from picric acid, &c.) With caustic soda an orange-yellow precipitate is formed, soluble on warming. In strong sulphuric acid the dinitronaphthol-sulphonates dissolve with pale yellow colour. In other reactions they resemble Manchester yellow, but do not volatilise or colour their paper envelope at 120° C.

NAPHTHOL YELLOW S; Naphthol Yellow; Citronin;[1] Acid Yellow S; Brilliant Yellow; &c., are names given to the potassium, sodium, ammonium, and calcium salts of dinitronaphthol-sulphonic acid. The free acid is also met with under the name of "naphthol yellow" (Levinstein).

Commercial naphthol yellow S varies much in character. Some qualities are practically pure, while others contain sodium sulphate and chloride in notable quantity. C. Rawson (*Jour. Soc. Dyers, &c.*, iv. 82) has proposed a method of assay depending on the precipitation of the colouring matter by a solution of night-blue, which is made by dissolving 10 grammes in 50 c.c. of glacial acetic acid, and diluting the liquid to 1 litre. The naphthol yellow is used as a solution containing 1 gramme per litre. The latter solution is added to 10 c.c. of the former until on filtration of a portion of the liquid it is found to have a faint yellow colour. The method is similar to that described for the determination of picric acid described on page 144. Two molecules of night-blue react with one of naphthol yellow.

Nitro-diphenylamines.

On treating diphenylamine with nitric acid it readily yields nitro-substitution products. The tetranitro-derivative, $[C_6H_3(NO_2)_2]_2NH$, mixed with a little of the dinitro-product, forms the colouring matter known as "Citronin."[1] On warming diphenylamine or methyl-diphenylamine with nitric acid, it yields hexanitro-diphenylamine, a body of strongly acid character, melting at 238°, the *ammonium salt* of which constitutes the "aurantia" of commerce.

AURANTIA, or Imperial Yellow, $[C_6H_2(NO_2)_3]_2N(NH_4)$, forms a reddish-yellow crystalline powder, or brownish-red crystals which decrepitate on heating and sometimes deflagrate slightly. Aurantia is easily soluble in water to form a solution which is red when concentrated, but yellow when diluted. On addition of hydrochloric acid, the aqueous solution yields a sulphur-yellow flocculent precipitate of free hexanitro-diphenylamine, and on filtering a nearly colourless liquid is obtained. The precipitate dissolves on agitation with ether. An acid solution of stannous chloride also precipitates the free acid, but the yellow precipitate becomes dark brown on boiling. Copper salts also turn the solution of aurantia brown. Solutions of aurantia are darkened or reddened by caustic alkalies, and if concentrated a dark red precipitate is produced. Solid aurantia is not changed in colour by strong sulphuric acid.

---

[1] The name citronin is used both for naphthol yellow S and the product obtained by acting with nitric acid on diphenylamine, as also for the azo-dye called azoflavine.

On the fibre, hydrochloric acid turns the colour due to aurantia a lighter yellow. Ammonia and caustic soda produce but little change. The dark brown coloration produced on warming with stannous chloride is the most characteristic reaction of aurantia.

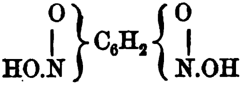
NITROSO-COLOURING MATTERS.

By treating an aqueous solution of phenol with potassium nitrite and acetic acid, a body is formed which was formerly supposed to be nitroso-phenol, $C_6H_4(NO).OH$, but which more recent research has shown may more correctly be regarded as quinonoxime, $C_6H_4O(NOH)$, or $C_6H_4\left\{\begin{array}{l} O \\ | \\ N.OH. \end{array}\right.$

Quinonoxime is best prepared by treating phenol dissolved in thirty parts of water with rather more than the theoretical quantity of nitrosulphonic acid, prepared by passing nitrous fumes into concentrated sulphuric acid. The crystals which separate are filtered off without delay. Quinonoxime forms a green solution in hot water, separating in nearly colourless needles by rapid cooling, or in thin, brownish-green plates if the liquid be cooled slowly. It dissolves in alkalies with brown colour, and on acidulating the solution separates as a nearly white amorphous precipitate, soluble in alcohol or ether with green colour.

Quinonoxime, if moist, rapidly turns brown on exposure to air. When heated to 120°–130° C. it decomposes with slight detonation. By ferricyanides in alkaline solution it is oxidised to paranitrophenol. When quinonoxime is dissolved in phenol, strong sulphuric acid added, and the liquid warmed to about 40° C., a dark cherry-red or brown solution is obtained, which on addition of water yields a flocculent brown precipitate, known as "Liebermann's phenol dye-stuff." This body dissolves in alkalies and sulphuric acid with fine blue colour, and has the formula, $C_6H_4(OH).N:(O.C_6H_5)_2$.

Quinone-dioxime. Dinitrosoresorcinol. $C_6H_2O_2(NOH)_2$ or



$$\left.\begin{matrix}O\\|\\HO.N\end{matrix}\right\}C_6H_2\left\{\begin{matrix}O\\|\\N.OH\end{matrix}\right.$$

. This body, which forms the commercial colouring matter known as *resorcin green* or *solid green*, is obtained in a manner similar to quinonoxime, substituting resorcinol for phenol. It forms yellowish-brown or green plates, or a greyish-brown powder. It dissolves with difficulty in cold water, but readily in hot. It deflagrates slightly when heated to 115°. Dinitrosoresorcinol has acid characters. It decomposes carbonates, and to some extent acetates, and forms a series of alkali-metal salts, of which the normal are soluble, and the acid, of the type $C_6H_2O_2(NOH)(NONa)$, are sparingly soluble, green, crystalline powders.

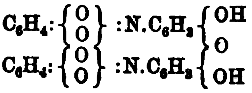
By the action of resorcinol and sulphuric acid on dinitrosoresorcinol, azoresorufin is formed, a body which is analogous to the Liebermann's dye-stuff (see above) obtained in a similar manner from phenol.[1]

Azoresorufin, $C_{24}H_{16}N_2O_7$,[2] is a substance which crystallises from hot hydrochloric acid in small, garnet-red prisms. It is nearly insoluble in water and alcohol. In strong sulphuric acid, azoresorufin dissolves with bluish-violet colour; with alkalies, particularly in alcoholic solution, it forms a carmine-red liquid with a splendid cinnabar-red fluorescence. This colour is so intense that azoresorufin may be used as a delicate reagent for alkalies, 0·000004 gramme of caustic soda being sufficient to pro-

---

[1] In practice, 1 part of resorcinol is dissolved in 5 parts of strong sulphuric acid, and the solution gradually treated with 8 parts of a nitrosulphonic acid made by gradually dissolving sodium nitrite in twenty times its weight of strong sulphuric acid. The fine blue solution is heated to 140° till violet, when it is cooled and diluted with water. The precipitate may be purified, if desired, by treating it with sodium carbonate, evaporating the solution to dryness, and treating the residue with alcohol, which dissolves the sodium compound of the colouring matter.

[2] Azoresorufin was formerly called diazo-resorufin, a name which suggests, without warrant, that it contains the diazo-group—N:N—; whereas its true constitution is probably expressed by the formula:—



$$\begin{matrix} C_6H_4:\left\{\begin{matrix}O\\O\end{matrix}\right\}:N.C_6H_3 \\ C_6H_4:\left\{\begin{matrix}O\\O\end{matrix}\right\}:N.C_6H_3\end{matrix}\left\{\begin{matrix}OH\\O\\OH\end{matrix}\right.$$

duce the reaction. Its extreme sensitiveness to alkalies renders azoresorufin unsuitable for dyeing, but this objection does not extend to its bromo-derivative.

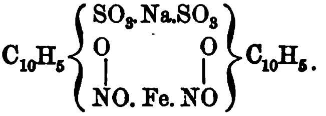
Hexabrom-azoresorufin (?) is produced by adding bromine to a solution of azoresorufin in caustic alkali. On acidulating the solution with hydrochloric acid the colouring matter is precipitated, and may be purified by crystallisation from toluene. It may be converted into the sodium or ammonium salt, the latter of which constitutes the colouring matter known as

FLUORESCENT RESORCIN BLUE, or *Bleu fluorescent.* This dye stuff crystallises in green lustrous needles, which are but slightly soluble in water or strong alcohol, but more readily in proof-spirit. The solutions are blue by transmitted and red by reflected light, and give a brown precipitate of hexabromresorufin on addition of a strong acid.

Fluorescent blue occurs in commerce as a 10 per cent. paste in which beetle-green crystals of the colouring matter may be recognised. It readily dyes silk in a neutral soap bath, the colour produced being blue, with a slight admixture of red and grey, and a characteristic red fluorescence, easily visible in artificial light. It is perfectly fast to light, washing, and acids, but ammonia and soda strip the fibre, forming blue solutions with strong red fluorescence. Strong hydrochloric acid changes the colour of fibres dyed with resorcin blue to brown.

LACMOID. Another blue colouring matter, sometimes called "resorcin-blue," can be obtained by slowly heating together 100 parts of resorcinol, 5 of sodium nitrite, and 5 of water. At 110° C. a vigorous reaction occurs, ammonia is evolved, and the mixture becomes red; when the melt is further heated to 115°–120° till the evolution of ammonia ceases, and the colour changes to blue. The mass is then dissolved in water and the solution filtered and precipitated by hydrochloric acid. The product is a glistening brown powder, which is insoluble in chloroform, benzene, or petroleum spirit, easily soluble in alcohol, wood spirit, and amylic alcohol, and less soluble in water and ether. The colouring matter was named by its discoverers (Traub and Hock, *Jour. Soc. Chem. Ind.*, iv. 297) lacmoid, owing to its behaving to acids and alkalies in a manner analogous to litmus, with the colouring matter of which they suggested it might be identical. R. T. Thomson, however, has shown (*Chem. News*, lii. 18 and 31) that well-marked differences exist, lacmoid being far less sensitive to weak acids than is the case with litmus. In this respect lacmoid resembles helianthin (methyl-orange), for which it may be substituted with advantage in certain cases. Thus it is superior to all other indicators for determining the carbonates of the earth-metals (temporary hardness of water, *Chem. News*, xlix. 34). In most cases, lacmoid paper is preferable to the solution, which when used should be made with proof-spirit and of 5 per cent. strength. Lacmoid paper can be employed in cases where the dark colour of the liquid renders methyl-orange unsuitable. Thus, bichromate of potassium, $K_2Cr_2O_7$, and the corresponding salt of sodium are exactly neutral to lacmoid, the chromates of neutral constitution, M_2CrO_4, being strongly alkaline in reaction. An admixture of 1 per cent. of K_2CrO_4 can be detected and estimated in $K_2Cr_2O_7$ by means of lacmoid paper, if, after immersion, the paper be washed to remove the strongly coloured liquid. The bodies represented by the following formulæ are also neutral to lacmoid :— $FeSO_4$, $FeCl_2$, $CuSO_4$, $CuCl_2$, $ZnSO_4$, H_3BO_3, H_3AsO_3, KH_2AsO_4, NaH_2PO_4, $NaHSO_3$. (Compare helianthin, phenolphthaleïn, congo-red and litmus.)

Naphthol Green B is the sodium-ferrous salt of nitrosobetanaphthol-sulphonic acid (Schäffer's acid),



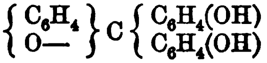
$$C_{10}H_5\left\{\begin{array}{ccc} & SO_3.Na.SO_3 & \\ O & & O \\ | & & | \\ NO. & Fe. & NO \end{array}\right\}C_{10}H_5.$$

It forms a dark green powder, which leaves, on ignition, a residue containing iron and sulphides. The colouring matter dissolves in water with yellowish-green coloration, the solution being unchanged by hydrochloric acid, but rendered bluish-green by alkalies. In concentrated sulphuric acid, naphthol green dissolves with yellowish-brown colour, the solution becoming yellow on dilution, and then giving a blue coloration or precipitate both with ferro- and ferri-cyanides.

AURIN AND ITS ALLIES.

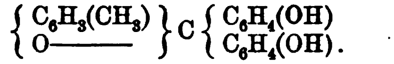
By heating phenol with oxalic and sulphuric acids a yellowish-red colouring matter is produced, which is known in commerce as aurin or rosolic acid. The nature of the reaction was long misunderstood, but later researches have shown that at least two homologous bodies had been previously confounded, namely :—

Aurin, or Pararosolic Acid, $C_{19}H_{14}O_3$, or



$$\left\{\begin{array}{l} C_6H_4 \\ O- \end{array}\right\}C\left\{\begin{array}{l} C_6H_4(OH) \\ C_6H_4(OH) \end{array}\right.;$$ and

Rosaurin, Rosolic Acid, or Methyl-aurin, $C_{20}H_{16}O_3$, or



$$\left\{\begin{matrix} C_6H_3(CH_3) \\ O\text{———} \end{matrix}\right\} C \left\{\begin{matrix} C_6H_4(OH) \\ C_6H_4(OH). \end{matrix}\right.$$

The formula expressing the formation of aurin is:—

$$3C_6H_6O + C_2H_2O_4 = C_{19}H_{14}O_3 + CH_2O_2 + 2H_2O.$$

Aurin and rosaurin may also be obtained by the action of nitrous acid on pararosaniline and rosaniline respectively:—

$$C_{20}H_{21}N_3O + 3HNO_2 = C_{20}H_{16}O_3 + 4H_2O + 3N_2.$$

Or a dilute solution of aniline hydrochloride may be treated with sodium nitrite, when diazorosaniline chloride is formed, and then on adding sulphuric acid and boiling rosolic acid is produced.

Conversely, when aurin and rosaurin are heated with aqueous ammonia under pressure to 200° C. they are reconverted into pararosaniline and aniline respectively:—$C_{19}H_{14}O_3 + 3NH_3 = C_{19}H_{19}N_3O + 2H_2O$.

From these reactions it appears that aurin and rosaurin are derivatives of triphenylmethane, $CH(C_6H_5)_3$.

Pure aurin may be obtained from the commercial product by passing ammonia gas through a saturated alcoholic solution of the latter, when steel-blue crystals of ammonium aurate, $C_{19}H_{12}O.(ONH_4)_2$, are deposited, the impurities remaining in solution. The washed precipitate may be decomposed by dilute hydrochloric or acetic acid, or simply exposed to the air, when ammonia volatilises and pure aurin remains.

When pure, aurin forms crystalline needles having an adamantine lustre and the colour of chromic acid, or else of a darker shade with a blue or greenish-blue reflection. Aurin is fusible, but not volatile without decomposition.

Commercial aurin or rosolic acid contains an atom or two of water, and is a dark amorphous substance with a beetle-green lustre. The powder is red.

Aurin and rosaurin are but slightly soluble in water, though their solutions having a reddish-yellow colour. They dissolve very readily in hot alcohol, somewhat more sparingly in cold, and are also moderately soluble in glacial acetic acid, phenol, creosote, and in ether, but are insoluble in benzene and carbon disulphide.

Aurin and rosaurin dissolve readily in solutions of ammonia and fixed alkalies to form solutions which are bluish-red when dilute and yellowish-red when concentrated. A characteristic change in the absorption-spectrum occurs on dilution.

Aurin and rosaurin have the property of combining both with acids and bases. The former compounds are the more definite; but ether extracts aurin and rosaurin from its acidulated solutions and not from its alkaline solutions.

Solutions of aurin are decolorised when heated with sodium amalgam, or caustic soda and zinc-dust, colourless hydraurin, $C_{19}H_{16}O_3$, being formed. The alkaline solution is also decolorised by heating with excess of potassium cyanide, and on cooling and acidulating white crystalline flocks of hydrocyanaurin, $C_{20}H_{15}NO_3$, are thrown down.

YELLOW CORALLIN. This colouring matter is prepared by treating 8 parts of pure phenol in the cold with 3·2 parts of strong sulphuric acid, and after some hours adding 4·8 parts of oxalic acid, and heating the whole to 110° for twenty-four hours. In addition to aurin and methyl-aurin, more or less oxidised aurin, $C_{19}H_{16}O_{31}$, and pseudo-rosolic acid or corallin-phthaleïn, $C_{20}H_{16}O_4$, are also produced, and a sublimate of phenyl oxalate has been observed to be formed. The melt is poured into water and purified by treatment with .boiling water. The product is yellow corallin, and forms a brown resinous substance having a green metallic lustre. It contains about 20 per cent. of aurin, besides crystalline derivatives of rosolic acid, and resinous bodies. Its reactions are identical with those of aurin. The soluble sodium salt of red corallin is also called "yellow corallin."

RED CORALLIN OR PEONIN is prepared by heating two parts of yellow corallin with one of strong ammonia to 120°–140° C., when one of the hydroxyl groups is replaced with formation of the substance, $C_{19}H_{13}O_2(NH_2)$, which is precipitated on pouring the liquid into water and acidifying. The product is "spirit soluble" red corallin; "water soluble" corallin being the ammonium salt. The first forms lumps with a metallic lustre; the latter a brownish-red porous mass, soluble in concentrated sulphuric acid with yellow colour. The red aqueous solution of the ammonium salt is unaltered by alkalies and precipitated yellow by acids. Basic lead acetate and aluminium acetate produce orange or yellow precipitates.

Eupittonic acid (page 72) has the constitution of a hexamethylaurin.

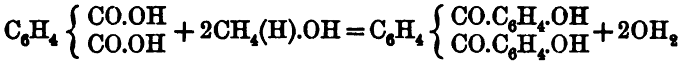
DETECTION OF AURIN, &c.

Aurin and its allies are readily recognised by their physical characters, and by dissolving in strong sulphuric acid with yellow colour, no vapours of bromine or iodine being evolved on heating, either with or without the addition of manganese dioxide. If not readily soluble in water alone, they dissolve in dilute ammonia with non-fluorescent purple-red colour, which is not removed by agitation with ether. On acidulating, the red solution is changed to yellow, a yellow precipitate being formed in strong solutions. This is readily soluble in ether, with yellow colour, and on separating the ethereal layer and agitating it with ammonia the latter acquires a deep red colour. Solutions of aurin are immediately decolorised by hypochlorites, or by boiling with zinc-dust and ammonia, the red colour being restored in the latter case on adding potassium ferricyanide.

Aurin and its allies are not now used in dyeing, as the yellow or orange-red shades produced are very perishable. The colouring matter on printed fabrics is turned yellow by acids, and readily removed by ammonia, the solution being purple-red. On acidulating this liquid with acetic acid, and heating in it a tuft of gun-cotton, the latter is dyed yellow.

PHTHALEÏNS.

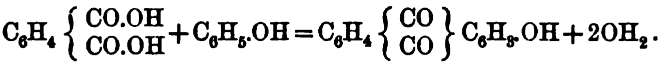
The phthaleïns are bodies produced by the reaction of phthalic acid or anhydride on phenols, with elimination of water. At a moderate temperature, two molecules of the phenol react with one of phthalic acid or anhydride, a "phthaleïn" being formed, thus:—



$$C_6H_4\left\{\begin{matrix}CO.OH\\ CO.OH\end{matrix}\right. + 2CH_4(H).OH = C_6H_4\left\{\begin{matrix}CO.C_6H_4.OH\\ CO.C_6H_4.OH\end{matrix}\right. + 2OH_2.$$

The product, phenol-phthaleïn, has the constitution of a dihydroxy-diphenyl-phthalide.[1]

At a higher temperature, by the reaction of one molecule of each body, oxyanthraquinone, a derivative of anthracene, is formed:—



$$C_6H_4\left\{\begin{matrix}CO.OH\\ CO.OH\end{matrix}\right. + C_6H_5.OH = C_6H_4\left\{\begin{matrix}CO\\ CO\end{matrix}\right\}C_6H_3.OH + 2OH_2.$$

As a class, the phthaleïns are weak acid bodies, nearly insoluble in water, but soluble in alcohol and readily so in ether. Their salts with the alkali-metals are soluble and strongly coloured. By the action of nascent hydrogen, the phthaleïns assimilate H_2 and are converted into the corresponding phthalins, which are colourless bodies absorbing oxygen from the air with re-formation of phthaleïns. The phthaleïns of phenol, resorcinol, and pyrogallol are the most important. The following table shows the constitution of those of greatest practical interest:—

---

[1] According to another view of its constitution, phenol-phthaleïn is a derivative of triphenyl-methane, $C(C_6H_5)_3H$, and hence is allied to aurin and pararosaniline.

Commercial Name.	Chemical Name or Nature.	Formula.
Phenol-phthaleïn.	Phenol-phthaleïn.	$C_6H_4\left\{\begin{array}{l}CO.C_6H_4(OH).\\CO.C_6H_4(OH).\end{array}\right.$
Resorcinol-phthaleïn.	Resorcinol-phthaleïn.	$C_6H_4\left\{\begin{array}{l}CO.C_6H_3(OH)_2.\\CO.C_6H_3(OH)_2.\end{array}\right.$
Fluoresceïn (page 165).	Anhydride of resorcinol-phthaleïn.	$C_6H_4\left\{\begin{array}{l}CO.C_6H_3(OH)\\CO.C_6H_3(OH)\end{array}\right\}O.$
Chrysolin (page 166).	Sodium salt of benzyl-fluoresceïn.	$C_6H_4\left\{\begin{array}{l}CO.C_6H_3(OC_7H_7)\\CO.C_6H_3(ONa)\end{array}\right\}O.$
Eosins (page 169).	Various derivations of fluoresceïn; *e.g.*, Cyanosin, the potassium salt of methyl-tetra-bromo-dichloro-fluoresceïn.	$C_6H_2Cl_2\left\{\begin{array}{l}CO.C_6HBr_2(OCH_3)\\CO.C_6HBr_2(OK)\end{array}\right\}O.$
Rhodamine (page 173).	...	$C_6H_4\left\{\begin{array}{l}CO.C_6H_3.N(C_2H_5)_2\\CO.C_6H_3.N(C_2H_5)_2\end{array}\right\}O.$
Galleïn (page 78).	Pyrogallol-phthaleïn.	$C_6H_4\left\{\begin{array}{l}CO.C_6H_2(OH)_3.\\CO.C_6H_2(OH)_3.\end{array}\right.$
Cœruleïn (page 78).	Anhydride of pyrogallol-phthaleïn.	$C_6H_4\left\{\begin{array}{l}CO.C_6H_2(OH)_2\\CO.C_6H_2(OH)_2\end{array}\right\}O.$

Phenol-phthaleïn. Dihydroxy-diphenyl-phthalide.

$$C_{20}H_{14}O_4 = C_6H_4\left\{\begin{array}{l}CO.C_6H_4(OH).^{p}\\CO.C_6H_4(OH).^{p}\end{array}\right.$$

As stated on page 163, phenol-phthaleïn results from the reaction of phenol on phthalic acid or anhydride.[1]

Phenol-phthaleïn is not used in dyeing, and derives its chief interest from the magnificent pink coloration which its solution acquires by the action of alkalies, the smallest trace of which may thus be detected. On the other hand, the weakest acids destroy the colour, so that such bodies as potassium stearate, potassium cyanide, and sodium bicarbonate ($NaHCO_3$) are neutral in their reaction to it.

The same is true of cold aqueous solutions of the bodies represented by the following formulæ:—$KHCO_3$, $Na_2S_2O_3$, Na_2SO_3, $NaHS$, Na_2HPO_4, Na_2HAsO_4, $NaNO_2$, K_2CrO_4, $K_2C_2O_4$, $KNaC_4H_4O_6$, $Na_3C_6H_5O_7$. In all these cases the point of neutrality is indicated extremely sharply, and the same remark applies to the titration of acetic, butyric, and valeric acids. No small advantage possessed by phenol-phthaleïn is that it reacts perfectly in alcoholic and even ethereo-alcoholic solution, and hence allows of the accurate titration of many insoluble organic acids, including palmitic, stearic, oleic, linoleic, ricinoleic, the acids of colophony (pinic, pimaric, sylvic), &c. The alkaloids have generally no marked alkaline reaction on phenol-phthaleïn, and hence the amount of acid in salts of morphine, quinine, cinchonine, quinidine, brucine, aniline, and urea, operating, if necessary, in alcoholic solution, can be ascertained by titration with standard acid, just as if no organic base were present.

---

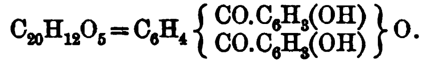
[1] Five parts of phthalic anhydride, ten of phenol, and four of concentrated sulphuric acid should be heated together to 120° C. for 10 hours. The product is boiled with water, and the residue dissolved in dilute soda. On filtering the liquid, the anhydride remains behind, while the phenol-phthaleïn itself is precipitated on treating the filtrate with acetic acid and a little hydrochloric acid. It may be purified by dissolving in alcohol, boiling with animal charcoal, and reprecipitating by diluting the liquid with boiling water.

The value of phenol-phthaleïn as an indicator of neutrality is completely vitiated by the presence of ammonium salts.

Phenol-phthaleïn is readily soluble in alcohol. A 1 per cent. solution keeps perfectly, and a few drops are sufficient for each titration.

Further information respecting the use of phenol-phthaleïn as an indicator of neutrality will be found in the section on "Litmus."

Fluoresceïn.



$$C_{20}H_{12}O_5 = C_6H_4\left\{\begin{matrix}CO.C_6H_3(OH)\\ CO.C_6H_3(OH)\end{matrix}\right\}O.$$

This body is the anhydride of resorcinol-phthaleïn, $C_{20}H_{14}O_6$ (see last page). It is prepared by heating three parts of phthalic anhydride and four of resorcinol to 200°–210° for one hour, or till no more steam is evolved and the melt has become solid.[1] The product is purified by solution in soda and addition of phosphate of sodium and chloride of calcium to the solution, when the phosphate of calcium carries down the impurities, and the fluoresceïn may be precipitated by acidulating the filtrate.

Fluoresceïn forms an amorphous yellow precipitate which becomes crystalline and yellowish-red on standing or drying, and then contains $C_{20}H_{12}O_5 + H_2O$. It is nearly insoluble in cold water, more readily in acidulated, and sparingly in hot water, to which it imparts a yellow colour. When freshly precipitated it dissolves readily in alcohol and ether, but is nearly insoluble in benzene and chloroform. The ethereal solution is pale yellow and non-fluorescent, while the yellowish-red alcoholic solution shows a green fluorescence.

Fluoresceïn is a feeble acid, dissolving in alkalies with dark red colour. The strong alkaline solution is not fluorescent, but on dilution it changes to reddish-yellow and yellow, and then exhibits a magnificent yellowish-green fluorescence, similar to that of uranium glass, and gives an absorption-spectrum with a broad dark band in the green. Even if the solution be so dilute as to appear colourless by transmitted light, the green bloom is still visible.[1]

---

[1] For a valuable description of the manufacture of fluoresceïn and eosin dyes, see a paper by O. Mühlhauser, *Jour. Soc. Dyers, &c.*, iii. 28, 63, translated from *Dingler's Polyt. Journal.*

When a solution of fluoresceïn in caustic soda is heated with zinc-dust the liquid becomes colourless and contains fluorescin, $C_{20}H_{14}O_5$. On filtering from the excess of zinc and exposing the liquid to the air, it gradually re-acquires its reddish colour, owing to the absorption of atmospheric oxygen and re-formation of fluoresceïn. Or if the colourless liquid be acidulated and agitated with ether, the fluorescin is dissolved, and on evaporating the ether is left as a colourless varnish, soluble without coloration in soda to form a liquid which rapidly turns red in the air from formation of fluoresceïn. The oxidation is immediate on addition of a ferricyanide to the alkaline liquid.

Fluoresceïn dyes silk and wool yellow, but the colours are not fast. It forms insoluble lakes with silver, lead, &c., which compounds are not poisonous, and hence may be used for colouring toys, india-rubber goods, &c.

BENZYL-FLUORESCEÏN, $C_{20}H_{10}O_3(OC_7H_7)OH$, is produced by heating benzyl-resorcinol with phthalic acid and strong sulphuric acid. Its sodium salt constitutes the dye-stuff known as

CHRYSOLIN or URANIN.[2] A reddish-brown powder possessing a greenish reflex. Its aqueous and alcoholic solutions are yellowish-brown, and exhibit a remarkable green fluorescence, which disappears with formation of a brown-yellow precipitate of benzyl-fluoresceïn on addition of acids. The precipitate is soluble in ether. The aqueous solution is darkened by alkalies, and the solid dye dissolves in strong sulphuric acid with yellow colour, and yields a yellow precipitate on dilution. With stannous chloride and with lead salts, chrysolin gives brilliantly coloured lakes. It dyes silk or wool a fast yellow, and is employed in

[1] The beautifully fluorescent fountain shown by I. Levinstein, in the Chemical Section of the Manchester Jubilee Exhibition, was fed by water containing 1 part per million of fluoresceïn. The intensity of the fluorescence may be employed for tracing the course of underground rivers and detecting the pollution of the water of wells by sewage, &c. By this means an underground connection was proved to exist between the Danube and the Ach, a small river flowing into Lake Constance.

[2] The name uranin is also applied to the sodium salt of fluoresceïn or methyl-fluoresceïn. It forms a yellowish-brown powder, the aqueous solution of which fluoresces yellowish-green.

cotton-dyeing for topping quercitron-yellow, the quercitron itself acting as a mordant.

Substituted Fluoresceïns. Eosins.

A series of interesting and practically important colouring matters can be obtained by substituting the halogens, nitryl, or the alcohol-radicals for some of the hydrogen atoms of fluoresceïn. The following is a tabular list of some of the more important bodies of this class:—

	Chemical Name or Nature.	Formula.	Commercial Name.
Soluble in Water.	Sodium salt of *Dibrom-fluoresceïn*. (Page 167.)	$C_6H_4\left\{\begin{array}{l}CO.C_6H_2BrONa\\CO.C_6H_2BrONa\end{array}\right\}O.$	Eosin, orange.
	Potassium, sodium or ammonium salt of *Tetrabrom-fluoresceïn*. Bromeosin. (Page 167.)	$C_6H_4\left\{\begin{array}{l}CO.C_6HBr_2OK\\CO.C_6HBr_2OK\end{array}\right\}O.$	Eosin, yellowish. Do. A or G. Do. B or B extra. Do. soluble.
	Potassium or sodium salt of *Tetraiodo-fluoresceïn*. Iodeosin. (See page 169.)	$C_6H_4\left\{\begin{array}{l}CO.C_6HI_2OK\\CO.C_6HI_2OK\end{array}\right\}O.$	Eosin, bluish. Pyrosin J or R. Erythrosin B. Primrose soluble.
	Sodium or ammonium salt of *Dibromo-dinitro-fluoresceïn*. Nitrobromeosin. (Page 169.)	$C_6H_4\left\{\begin{array}{l}CO.C_6HBr_2ONa\\CO.C_6H(NO_2)_2ONa\end{array}\right\}O.$	Eosin, BN. Safrosin. Eosin scarlet.
	Potassium salt of *Tetrabromo-dichloro-fluoresceïn*. Bromochloreosin. (Page 169.)	$C_6H_2Cl_2\left\{\begin{array}{l}CO.C_6HBr_2OK\\CO.C_6HBr_2OK\end{array}\right\}O.$	Phloxin.
	Potassium or sodium salt of *Tetraiodo-dichloro-fluoresceïn*. Iodochloreosin. (Page 169.)	$C_6H_2Cl_2\left\{\begin{array}{l}CO.C_6HI_2OK\\CO.C_6HI_2OK\end{array}\right\}O.$	Rose Bengale. Bengal red.
Spirit Soluble.	Sodium *methyl salt of Tetrabrom-fluoresceïn*. Methyl-eosin. (Page 170.)	$C_6H_4\left\{\begin{array}{l}CO.C_6HBr_2OCH_3\\CO.C_6HBr_2ONa\end{array}\right\}O$	Eosin soluble in alcohol. Erythrin.
	Potassium *ethyl salt* of *Tetrabrom-fluoresceïn*. Ethyl-eosin. (Page 169.)	$C_6H_4\left\{\begin{array}{l}CO.C_6HBr_2OC_2H_5\\CO.C_6HBr_2OK\end{array}\right\}O.$	Ethyl-eosin. Rose JB. Primrose.
	Potassium *methyl salt of Tetrabromo-dichloro-fluoresceïn*. Methyl-phloxin. (Page 169.)	$C_6H_2Cl_2\left\{\begin{array}{l}CO.C_6HBr_2OCH_3\\CO.C_6HBr_2OK\end{array}\right\}O.$	Cyanosin.

TETRABROMFLUORESCEÏN, or ACID EOSIN, $C_{20}H_3Br_4O_5$, is prepared by gradually adding 24 parts of bromine to 10 parts of fluoresceïn dissolved in eight times its weight of strong alcohol. When half the bromine has been added changes from reddish-brown to a very dark brown colour. This marks the formation of the dibromo-derivative,[1] which is easily soluble in alcohol. On continuing the addition of bromine the tetrabromfluoresceïn separates as a brick-red crystalline precipitate, which is washed with a little alcohol and then with water. An alternative method of preparation is to mix a solution of fluoresceïn in caustic soda with a solution of the calculated amount of bromine in caustic soda, and then acidulate the liquid with hydrochloric acid, when the tetrabromfluoresceïn is precipitated.

---

[1] The sodium salt of dibromfluoresceïn, always mixed with more or less of the tetrabrominated derivative, is known in commerce as *eosin orange*.

Tetrabromfluoresceïn closely resembles fluoresceïn itself. It is nearly insoluble in water, and its reddish-yellow solution in alcohol is not fluorescent (distinction from fluoresceïn). It is a well-defined dibasic acid, the salts of which are decomposed by mineral acids, but only imperfectly by acetic acid.

By cautious treatment with caustic potash, acid eosin yields the potassium salt, $C_{20}H_6Br_4O_5K_2 + 6aq$, which is known in commerce as *soluble eosin,* and forms a red powder or brownish-red crystals with a blue or yellowish-green reflection. It is not easily soluble in absolute alcohol, but dissolves completely in two or three times its weight of water to form a reddish-yellow solution. This on dilution becomes rose-coloured and exhibits an intense yellowish-green fluorescence, which is rendered still stronger by the addition of alcohol. The absorption-spectrum shows a broad dark band in the green, destroyed by mineral acids, but not by acetic acid. On adding hydrochloric acid the solution becomes yellow, and on heating gives a yellow precipitate of tetrabromfluoresceïn, which may be extracted by ether and removed from the ethereal solution by agitation with an alkali.

The sodium salt of the tetrabromfluoresceïn is an article of commerce under the name of *Eosin C*, or in the form of garnet-red crystals as *Eosin B extra.* It closely resembles the potassium salt. The ammonium salt, known as *Eosin B*, of a *red* appearance, is prepared by the direct action of ammonia gas on tetrabromfluoresceïn.

By the addition of a soluble salt of eosin to solutions of the heavy metals, sparingly soluble or insoluble lakes are obtained as precipitates. Silver gives red, and zinc, cobalt, iron, manganese, bismuth, and tin reddish-yellow lakes.

A bright vermilion lake may be obtained by mixing the solution of eosin with starch or kaolin and precipitating with alum. If excess of alkali be previously added to the solution, the precipitate obtained is carmine-red, and with still more alkali a pink lake results. For yellowish shades sulphate of zinc or magnesium should be used in conjunction with alum.

Vermilionette is a brilliant lake obtained by precipitating eosin by lead acetate. Lighter shades are obtained by adding soda. A very bright vermilion-coloured product is obtained by stirring up red-lead with an alkaline solution of eosin and then adding lead acetate to complete precipitation. Basic chromate of lead (chrome-red) gives even a brighter red than red-lead. Vermilionette sometimes contains a considerable proportion of barium sulphate or other diluent.

Tetraiodfluoresceïn, or Iodeosin, $C_{20}H_8I_4O_5$, is prepared by mixing solutions of fluoresceïn and iodine in caustic soda, and then adding acetic acid. Its alkaline salts are sold as *eosin blue-shade* (soluble in water), *eosin J*, *erythrosin*, *erythrosin B*, *pyrosin B*, *iodeosin B*, *dianthin B*, and *soluble primrose*.[1] The sodium salt is brown-red and the ammonium salt light brick-red. Their aqueous solutions are not fluorescent (distinction from the brominated eosins), and on treatment with zinc-dust and ammonia the iodine is eliminated and a colourless solution of fluorescin obtained, turning red on exposure to air, with formation of fluoresceïn (see page 166).

Dibromo-dinitrofluoresceïn, or Nitrobromeosin, $C_{20}H_8(NO_2)_2Br_2O_5$, is produced by the action of dilute nitric acid on tetrabromfluoresceïn dissolved in glacial acetic acid, or by acting with bromine on dinitrofluoresceïn in alcoholic solution. The salts are known in commerce as *safrosin*, *eosin scarlet*, *daphnin*, and *eosin BN*. The potassium and sodium salts are dark brown or green powders, while the ammonium salt is red. A mixture of bromonitrofluoresceïn with the di- and tetra-nitro-derivatives is known as *lutécienne*. *Rubeosin* is a nitrochlorofluoresceïn, obtained by the action of nitric acid on *aureosin*, which is itself a chlorinated fluoresceïn.

Tetrabromo-dichlorofluoresceïn, $C_{20}H_6Cl_2Br_4O_5$. In all the substituted fluoresceïns hitherto described the replaced hydrogen belongs to the resorcinol residue, but eosins may also be prepared in which the hydrogen atoms of the phthalic acid residue are replaced. Thus when dichlorphthalic acid reacts on resorcinol a dichlorofluoresceïn is obtained, and by brominating or iodinating this body other colouring matters result. *Rose Bengale* and *phloxin* are dyes of this kind, the former being the potassium or sodium salt of tetraiodo-dichlorofluoresceïn, and the latter the potassium salt of tetrabromo-dichloro- (or tetrachloro-) fluoresceïn (page 164). *Cyanosin* is the potassium salt of the methyl or ethyl ether of phloxin.

Ethers of substituted Fluoresceïns. The methyl and ethyl ethers of tetrabromfluoresceïn are obtained by heating eosin with methyl or ethyl alcohol and sulphuric acid, by heating acid eosin with methyl or ethyl bromide, or by brominating fluoresceïn in hot alcohol, when etherification and bromination occur simultaneously. The potassium salt of ethyl-tetrabromfluoresceïn is a red crystalline substance with a greenish reflex. It has found a considerable application in silk-dyeing, and is known as *spirit-eosin*, *ethyl-eosin*, *rose JB.*, *spirit-primrose*, &c. *Methyl-eosin* is of very similar character.

---

[1] Some of these names are applied to the alkaline salts of a di-iodfluoresceïn, $C_{20}H_{10}I_2O_5$.

Methyl- and ethyl-eosin are sparingly soluble in water and insoluble in absolute alcohol, but they dissolve easily in proof-spirit, the dilute solutions having a beautiful fluorescence.

Benzyl-fluoresceïn, or *chrysolin*, has already been described (page 166).

REACTIONS OF THE EOSINS.

In referring to the various substituted fluoresceïns, the systematic names are inconveniently long, while the commercial names are not always sufficiently distinctive. In such cases the terms bromeosin, iodoeosin, ethyl-eosin, &c., may be used with advantage.

The fluorescence of the eosins is most intense in alcoholic solutions (preferably containing a little free ammonia). It is strongest in the eosin-ethers (eosins soluble in alcohol), and then in bromeosin. Nitrobromeosin (safrosin) is but slightly fluorescent, but somewhat more so in presence of ammonia, while iodeosin does not fluoresce at all in aqueous and but little in alcoholic solution.

The absorption-spectra of aqueous and ammoniacal solutions of the eosins have been studied by C. H. Bothamley (*Jour. Soc. Chem. Ind.*, vi. 422), and exhibit some interesting peculiarities.

The eosins dissolve in cold concentrated sulphuric acid with yellow or orange colour, which generally becomes darker on heating. Bromeosin and nitrobromeosin are turned dark red, and on adding water a new colouring matter separates out in dark flakes. On heating iodeosin with strong sulphuric acid, iodine is liberated, and bromine vapours are evolved from brominated eosins, especially if manganese dioxide be added.

On adding hydrochloric acid to solutions of the eosins, the corresponding free substituted fluoresceïns are precipitated. In all cases the precipitates are soluble in ether, and on agitating the separated ethereal solution with soda or ammonia the eosin passes into the alkaline liquid with characteristic colour, and usually with fluorescence.

The following table shows the comparative characters of the principal substituted fluoresceïns:—

Name.	Solubility.	Colour of Solution.	Fluorescence of Solution.	Colour produced on Silk.	Behaviour with H_2SO_4.	Precipitate with HCl.
Eosin. Bromeosin. Eosin G.	Soluble in water; not stripped from fibre by alcohol.	If sufficiently dilute, crimson or cherry-red.	Yellowish-green; best observed in dilute solution.	Rose-red.	Yellow. On adding MnO_2 and heating, Br vapours evolved.	Orange-yellow.
Iodeosin. Eosin J. Erythrosin.	Soluble in water.	Crimson or bluish-red.	None or trifling.	Purple-red.	Yellow. On heating, with or without MnO_2, violet vapours of iodine are evolved.	Orange-red.
Nitrobromeosin. Safrosin.	Soluble in water.	Cherry-red or bluish-red.	Faintly yellowish-green.	Red.	Golden-yellow. Red vapours on adding MnO_2 and heating.	Straw-yellow or brownish-yellow, soluble in ether with yellow colour.
Bromo-chlor-eosin. Phloxin.	Soluble in water. Stripped from fabric by water, but not by alcohol.	Crimson or bluish-red.	Light or yellowish-green.	Rose-pink.	Yellow. On adding MnO_2 and heating, Br vapours evolved.	Flesh-coloured, soluble with yellowish-brown colour in ether.
Iodochlor-eosin. Bengal red.	Soluble both in water and alcohol.	Aqueous, bluish-red. Alcoholic, red.	Aqueous, not fluorescent. Alcoholic, golden-yellow.	Rose.	Orange. On heating, with or without MnO_2, violet vapours of iodine are evolved.	Ponceau-red, soluble in ether with yellow colour.
Methyl-eosin. Erythrin.	Scarcely soluble in water. Dissolved by weak alcohol.	Cherry-red or purple-red.	Green-yellow.	Purple-red.	Lemon-yellow or orange. Br vapours evolved on heating.	Red precipitate, or yellow non-fluorescent solution giving red precipitate on adding water.
Ethyl-eosin. Rose JB.	Scarcely soluble in cold water; readily in weak alcohol. Fabric stripped accordingly.	Cherry-red or bluish-red.	Strong green-yellow.	Purple-red.	Lemon-yellow or orange. Br vapours evolved on heating.	Yellow solution, giving fine red precipitate on adding water.
Methyl-phloxin. Cyanosin.	Insoluble in water; soluble in weak alcohol.	Reddish-blue.	Orange-yellow or brick-red.	Rose.	Brownish-yellow solution. Br vapours evolved with MnO_2.	Orange non-fluorescent solution, precipitated red on adding water.
Chrysolin. Uranin.	Soluble in water.	Yellow or yellowish-brown.	Yellowish-green.	Yellow.	Yellow; yellow precipitate on dilution.	Yellow, flocculent; fluorescence destroyed.

R. Benedikt (*Jour. Soc. Chem. Ind.*, ii. 170) has published a systematic scheme for the examination and identification of the various eosin dyes. Besides noting the solubility of the substance, the colour and the fluorescence of the solution, and the shade produced on silk, he notes the behaviour of the colouring matter when reduced. For this purpose, Benedikt directs that a few drops of a moderately concentrated solution of the dye should be diluted with water, and shaken in the cold with small quantities of zinc-dust and ammonia. All eosins are rapidly decolorised by this treatment. The decolorised and filtered solution usually reoxidises very gradually on exposure to the air, but more rapidly if it be well boiled till a copious precipitation of hydrated oxide of zinc occurs, and the liquid be then treated with sufficient hydrochloric acid to dissolve this precipitate, and an excess of ammonia again added. Another means of discrimination employed by Benedikt consists of treating a little of the colouring matter with a strong solution of caustic potash (1·3 sp. gr.).

By the reduction-test, *Eosin G* (bromeosin) gives a nearly colourless filtrate immediately after treatment with zinc and ammonia, being reduced to colourless tetrabromfluorescin. After boiling the liquid and treating with acid and ammonia as described above, the solution becomes cherry-red or crimson, with yellowish-green fluorescence; or, in other words, the original colouring matter is re-formed. With potash solution, bromeosin gives in the cold an orange-red solution, which on boiling becomes purple-red, violet, and pure blue, with a *strong* green fluorescence. If the boiling has been continued long enough, the characters are unchanged by dilution.

Eosin J (iodeosin) loses its iodine when treated with zinc-dust and ammonia, and is converted into colourless fluorescin, which on oxidation, boiling, &c., is converted into fluoresceïn, the solution of which is reddish-yellow with a strong green fluorescence. The production of a highly fluorescent solution from a non-fluorescent one by reduction and subsequent oxidation is highly characteristic of iodeosin. On boiling with potash, eosin B first turns purple-red and then blue-violet, with a feeble green fluorescence. On dilution, the liquid becomes purple-red.

Safrosin (nitrobromeosin), on treatment with zinc-dust and ammonia, is reduced to colourless fluorescin, and the NO_2 groups are simultaneously reduced. The filtered liquid oxidises again with great rapidity, with formation of a cherry-red, non-fluorescent solution. With potash, safrosin becomes lighter and yellower, and on boiling turns olive-green, without fluorescence. When a little solid safrosin is heated on platinum foil, it swells up enormously after the manner of a "Pharaoh's serpent."

The *spirit-soluble eosins* behave with zinc and ammonia like bromeosin. They are insoluble in strong potash solution in the cold, but on boiling the reactions of bromeosin are gradually produced.

The eosins are often found in admixture with other colouring matters. Thus *nepaline* and *imperial scarlet* are mixtures of eosins with naphthol-yellow (see page 154), and *coccine* is a mixture of safrosin and aurantia. Such mixtures yield scarlets which are employed as cochineal substitutes. Naphthol-yellow and aurantia differ from the eosins in yielding colourless solutions by treatment with zinc and hydrochloric acid, which solutions do not again become coloured on exposure to air, either with or without the addition of ammonia or sodium acetate. When heated, the nitro-compounds deflagrate without disengaging coloured vapours. To induce deflagration it is sometimes necessary to mix the substance with a little oxide of lead.

Aurin and its allies present a somewhat close analytical resemblance to the eosins; but their ammoniacal solutions are not fluorescent, and no bromine or iodine vapours are evolved on heating the substance with sulphuric acid and manganese dioxide.

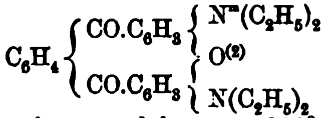
The eosins produce on silk and wool all shades of colour from a reddish-orange to a cherry-red and purple. The yellowish shade is produced by eosin G, and the bluest by bengal red. For dyeing cotton with eosins, the fabric is mordanted with alumina or tin for yellow shades, and with lead salts for blue shades. The colours produced are not so fast as those on wool or silk, and are affected by light.

The eosins soluble in water are slightly removed when *fibres* dyed with them are treated with warm water, especially if a little ammonia be added. Spirit-soluble eosins are not affected by water, but are dissolved from the fibre by alcohol, which leaves the eosins soluble in water. Concentrated potash solution acts as on the solid dyes, warm solution of bleaching powder discharges the colour, and sulphuric acid turns the fibre yellow or orange. Hydrochloric acid and acidulated stannous chloride decolorise or turn the fibre yellow.

Phthaleïns from Amidophenols.

Very recently, several colouring matters have appeared in commerce which are obtained by the reaction of phthalic anhydride on amidophenols or their allies. The representative member of this group of bodies is:—

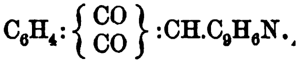
RHODAMINE,



$$C_6H_4\left\{\begin{matrix} CO.C_6H_3 \\ \\ CO.C_6H_3 \end{matrix}\right. \left\{\begin{matrix} N'''(C_2H_5)_2 \\ O^{(2)} \\ N(C_2H_5)_2 \end{matrix}\right.$$

. This body is formed by heating, for several hours at 200°, one molecule of phthalic anhydride with two of diethyl-meta-amidophenol. The commercial product is a hydrochloride of the base, and forms a red powder, readily soluble in water with fine crimson colour and a characteristic yellow fluorescence, which disappears on heating the solution to about 90° and is restored on cooling. Acids turn the colour of the liquid somewhat yellower, and alkalies slightly bluer. Tannic acid, in presence of sodium acetate, gives a bright crimson precipitate of rhodamine tannate which is not fast to light, but if tartar-emetic be also present the compound precipitate formed resists light very well. With stannous chloride, an aqueous solution of rhodamine gives a characteristic cinnabar-red precipitate, which, while still in a fine state of division, transmits a bright blue light (E. Knecht, *Jour. Soc. Dyers, &c.*, iv. 96). In strong sulphuric acid, rhodamine dissolves with yellow colour, changing to red on dilution with water. Rhodamine dyes silk and wool a pink colour, with a marked orange fluorescence. The dye stands light and soaping fairly well. It may be mordanted on cotton with turkey-red oil, or tannic acid and tartar-emetic. The colours obtained are fluorescent.

Quinoline Yellow. By heating quinaldin with phthalic anhydride and chloride of zinc, a phthaleïn is formed of the composition:—



$$C_6H_4:\left\{\begin{matrix}CO\\CO\end{matrix}\right\}:CH.C_9H_6N.$$

The product forms a yellow powder, which is insoluble in water, but difficultly soluble in alcohol, to form a yellow solution. In strong sulphuric acid the dye dissolves with yellowish-red colour, the solution giving a flocculent yellow precipitate on dilution. By sulphonation, quinoline yellow yields a disulphonic acid, the sodium salt of which contains $C_6H_4:(CO)_2:CH.C_9H_4(SO_3Na)_2N$, and is known as *water-soluble quinoline yellow*. It forms a bright yellow powder, dissolving easily in water with intense yellow colour, which is unaltered by dilute acids but is turned somewhat darker by ammonia. The dye is not applicable to cotton. On silk and wool, in a bath acidulated with sulphuric acid, it yields very pure shades of yellow, which stand light fairly well.

Azoeosin is a colouring matter of which the composition and mode of manufacture have not been made public. The commercial product forms a scarlet powder, readily soluble in water with scarlet colour, but without fluorescence. Ammonia turns the solution orange, and hydrochloric acid produces a crimson precipitate. In strong sulphuric acid the dye dissolves with deep cherry-red colour. On wool, azoeosin produces a brilliant scarlet, which stands light well, and is not easily affected by soaping (E. Knecht, *Jour. Soc. Dyers, &c.*, iv. 96).

AZO-COMPOUNDS AND COLOURING MATTERS.[1]

Of late years a series of very brilliant and fast dyes have come into use, which are generically known as azo-dyes.

All these substances contain the divalent group —N : N—. If both of the free bonds be satisfied by the radical phenyl the substance known as azo-benzene, $C_6H_5.N : N.C_6H_5$, results; or if the two radicals be not identical a "mixed" azo-compound results, such as may be typified by benzene-azo-toluene, $C_6H_5.N : N.C_7H_7$.

Azobenzene. $C_6H_5.N_2.C_6H_5$.

This body is prepared by the reduction of nitrobenzene with nascent hydrogen. Acetic acid and iron may be employed as the reducing agent, or preferably an alkaline reagent, such as zinc and alcoholic potash, sodium stannite, or sodium amalgam. If sodium amalgam be employed, the intermediate product azoxy-benzene is first obtained, while too-long continued treatment causes the formation of hydrazobenzene and the isomeric body benzidine, and the former of these may in turn be converted into aniline. These bodies form a continuous series, thus:—

Nitro-benzene,	$C_6H_5NO_2 \times 2 = C_{12}H_{10}N_2O_4$
Azoxy-benzene, . . .	$C_{12}H_{10}N_2O$
Azo-benzene, ...	$C_{12}H_{10}N_2$
Hydrazo-benzene, . . .	$C_{12}H_{12}N_2$
Amido-benzene(aniline),	$C_6H_7N \times 2 = C_{12}H_{14}N_2$.

By treating aniline with potassium permanganate, the reverse series of reactions may be obtained, at least so far as oxidation to azoxy-benzene; and among the secondary products is found *aniline black*, which has the same percentage composition as azo-benzene.

Azobenzene crystallises in large yellowish-red laminæ, sparingly soluble in water, but readily in alcohol and ether. The alcoholic solution has an intense yellow colour, but no dyeing powers. Azobenzene melts at 65°·5, and distils at 293°. Treated in alcoholic solution with sulphuretted hydrogen, it is converted into hydazobenzene. With bromine, azobenzene forms the additive compound $C_{12}H_{10}Br_2N_2$, and with nitric acid reacts to form mono- and di-nitro-derivatives. *Nitro-azobenzene*, $C_6H_5.N_2.C_6H_4(NO_2)$, can be reduced to amido-azobenzene, $C_6H_5.N_2.C_6H_4(NH_2)$, and this on treatment with nitrous acid and warm water yields oxyazobenzene, $C_6H_5.N_2.C_6H_4(OH)$.[1] These bodies dye silk or wool orange or yellow, but offer little resistance to the action of acids.

---

[1] The author is indebted to Professor R. Meldola for an advance-sheet of his article on "Azo-Colouring Matters," contributed to Thorpe's *Dictionary of Technical Chemistry*. A very complete list of the azo-dyes, with their formulæ and chemical reactions, has been published by Schultz and Julius (*Chemische Industrie*, 1887).

Diazobenzene Compounds. $C_6H_5.N:N.X$.

When the free bond of the second nitrogen atom of the group —N : N— is satisfied by a simple atom or an acid or basic group, instead of by a hydrocarbon radical, the substance is said to be a "diazo-compound." Thus the body represented by the formula $C_6H_5.N:N.Cl$ is called diazo-benzene chloride,[2] and is the type of a large number of interesting bodies.

Free diazobenzene is not known, nor does the hydride, $C_6H_5.N_2.H$, appear to be obtainable. The hydroxide, $C_6H_5.N_2.OH$, is a highly unstable, explosive, yellow oil, which reacts with acids to form a highly interesting series of salts. They are mostly colourless, crystalline bodies, which turn brown rapidly on exposure to air. They are readily soluble in water, sparingly in alcohol, and are precipitated from their alcoholic solutions by ether. Most of them are unstable, and decompose with explosion when heated or struck. The chlorochromate explodes more violently than nitroglycerin. By many reagents they are decomposed in a peculiar manner, usually with evolution of free nitrogen, as in the following examples:—

1. $\underset{\text{Diazo-bromide}}{C_6H_5.N_2.Br} + H_2O = \underset{\text{Phenol}}{C_6H_5.OH} + N_2 + HBr.$
2. $\underset{\text{Diazo-nitrate}}{C_6H_5.N_2.NO_3} + \underset{\text{Alcohol}}{C_2H_5OH} = \underset{\text{Benzene}}{C_6H_5H} + N_2 + HNO_3 + \underset{\text{Aldehyde}}{C_2H_4O}.$
3. $\underset{\text{Diazo-acid sulphate}}{C_6H_5.N_2.HSO_4} + HI = \underset{\text{Phenyl iodide}}{C_6H_5I} + N_2 + H_2SO_4.$
4. $\underset{\text{Diazo-chloride}}{C_6H_5.N_2.Cl} + Cu_2Cl_2 = \underset{\text{Phenyl chloride}}{C_6H_5Cl} + N_2 + CuCl_2.$[3]
5. $\underset{\text{Diazo-perbromide}}{C_6H_5.NBr:NBr_2} + C_2H_5.OH = \underset{\text{Phenyl bromide}}{C_6H_5Br} + N_2 + C_2H_4O + 2HBr.$

Diazobenzene Chloride, $C_6H_5.N_2.Cl$, is obtained in solution by gradually adding sodium nitrite to an ice-cold, dilute solution of one molecule of aniline and two of hydrochloric acid, the liquid being well stirred during the addition. The conclusion of the reaction is known by the evolution of nitrous acid, recognisable by its turning blue a piece of paper moistened with a solution of potassium iodide and starch and held over the liquid. Diazobenzene chloride is only known in solution, which undergoes decomposition when heated, but it forms crystalline compounds with platinic and stannic chlorides.

---

[1] This body is preferably called hydroxy-azobenzene. It must not be confounded with azoxy-benzene, $\left.\begin{matrix}C_6H_5.N\\C_6H_5.N\end{matrix}\right\}O$.

[2] Hence azobenzene, $C_6H_5.N:N.C_6H_5$, is diazobenzene phenylide.

[3] By substituting cuprous bromide, iodide, or cyanide for the chloride, the corresponding haloid compounds of phenyl may be obtained. The cyanide reacts with caustic potash to form potassium benzoate, C_6H_5COOK, and ammonia.

Diazobenzene Nitrate, $C_6H_5.N_2.NO_3$, is prepared by passing a slow stream of nitrogen trioxide gas (prepared from starch or arsenious oxide and nitric acid) into a paste of aniline nitrate and water,[1] cooled by immersion in a mixture of ice and salt, until the addition of caustic alkali to a sample quantity no longer liberates aniline in oily globules. The liquid is filtered, and the diazobenzene nitrate precipitated from the filtrate by adding three volumes of alcohol and some ether. Diazobenzene nitrate separates in yellow needles which are readily soluble in water, and slightly so in alcohol, but insoluble in ether. In the dry state, when gently heated or struck, it explodes more violently than fulminating mercury, and hence should be preserved under ether.

Acid Diazobenzene Sulphate, $C_6H_5.N_2.HSO_4$, is obtained by adding diluted sulphuric acid (1 : 2) to a concentrated aqueous solution of the last salt. Alcohol (3 volumes) and ether are then added, and the heavy liquid which separates redissolved in strong alcohol and precipitated by adding ether, the process being repeated till the sulphate separates in a crystalline form. The salt forms white, deliquescent prisms, which decompose in the air and detonate at about 100°.

Diazobenzene-sulphonic Acid, $C_6H_4\left\{\begin{matrix}.N:\\ .SO_3.\end{matrix}\right\}:N$. This body, of which three modifications exist, is not well named, as it is really the anhydride of the true sulphonic acid, $C_6H_4(SO_3H).N_2.OH$. The para-compound, which is the only one of practical importance, is obtained by adding rather more than the calculated quantity of sodium nitrite to a solution of sulphanilic acid (para-amidobenzene-sulphonic acid), $C_6H_4(SO_3H).NH_2$, in dilute caustic soda, and pouring the mixture into cooled, dilute sulphuric acid. The diazo-sulphonic acid separates in white crystals, insoluble in cold water, but readily soluble at 60°–70°. It is decomposed by water at a higher temperature, with formation of para-phenolsulphonic acid (page 5), while boiling alcohol converts it into benzene-sulphonic acid, $C_6H_5.SO_3H$.

DIAZO-AMIDOBENZENE, $C_6H_5N:N.NH.C_6H_5$. This body is formed when nitrous gas is passed into a solution of aniline in alcohol, and may be regarded as resulting from the action of aniline (amidobenzene) on diazobenzene hydroxide :—$C_6H_5.N_2.OH + NH.H.C_6H_5 = C_6H_5.N_2.NH.C_6H_5 + H_2O$. Diazo-amidobenzene is also formed when a cold concentrated solution of diazobenzene nitrate is dropped gradually into strong ammonia or mixed with aniline; or by adding a solution of diazobenzene chloride to aniline kept cool, and treating the product with sodium acetate, when the diazo-amidobenzene is thrown down as a yellow precipitate. It may be obtained more directly by adding gradually a cooled solution of sodium nitrite to a mixture of one molecule of aniline and one of aniline hydrochloride, when it is precipitated. Diazo-amidobenzene crystallises in golden yellow scales, melts at 91°, and detonates at a higher temperature. It is insoluble in water, but is dissolved easily by ether, benzene, or hot alcohol.

---

[1] $C_6H_5NH_2.HNO_3+HNO_2=C_6H_5.N_2.NO_3+2H_2O$.

Diazo-amidobenzene does not readily unite with acids, though a chloroplatinate is obtainable. By nitric acid containing nitrous acid, diazo-amidobenzene is converted into diazobenzene nitrate; by strong hydrochloric acid into aniline hydrochloride, phenol, and nitrogen.

Amidoazo-Compounds.

When diazo-amidobenzene is heated in the dry state in presence of aniline and a little aniline hydrochloride, it undergoes a molecular transformation into amido-azobenzene or *aniline yellow*, identical with the body obtained by the reduction of nitro-azobenzene :[1]—$C_6H_5.N_2.NH(C_6H_5) = C_6H_5.N_2.C_6H_4(NH_2)$.

It is important to notice the leading differences between diazo-amidobenzene and the metameric body amido-azobenzene. Thus the latter is a well-defined base, which on heating with an acid forms a salt which gives a red colour to the aqueous solution; while the former when similarly treated is decomposed into phenol, nitrogen, and aniline (hydrochloride).

If (instead of aniline) a solution of meta-phenylenediamine[2] be poured into a very dilute solution of diazobenzene chloride, the hydrochloride of diamido-azobenzene or *chrysoïdine* separates as a sparingly soluble precipitate :—$C_6H_5.N_2.Cl + C_6H_4(NH_2) = C_6H_5.N_2.C_6H_3(NH_2)_2HCl$.

---

[1] Diazobenzene chloride reacts with the secondary monamines to form diazoamido-substitution products. Thus with diethylamine, diethyldiazo-amidobenzene results :—$C_6H_5.N_2.Cl + HN(C_2H_5)_2 = C_6H_5.N_2.N(C_2H_5)_2 + HCl$. With a tertiary monamine a different reaction results, a substituted amidoazo-compound being formed. Thus diazobenzene chloride and dimethylaniline give the hydrochloride of dimethyl-amido-azobenzene (page 180), $C_6H_5.N_2.Cl + C_6H_5N(CH_3)_2 = C_6H_5.N_2.C_6H_4.N(CH_3)_2.HCl$. The primary amines of naphthalene react in a similar manner.

[2] META-PHENYLENEDIAMINE, $C_6H_4(NH_2)_2$, may be obtained by the reduction of dinitrobenzene, $C_6H_4(NO_2)_2$, produced by treating benzene with a mixture of fuming nitric and strong sulphuric acids. 250 grammes of iron filings are shaken in a flask with 15 c.c. of hydrochloric acid, 50 grammes of

On adding potassium nitrite to a solution of a neutral salt of meta-phenylenediamine, a brown precipitate (or in very dilute solutions, a brown coloration) is produced, which is due to the formation of triamido-azobenzene or *phenylene-brown*, $C_6H_4(NH_2).N_2.C_6H_3(NH_2)_2$.

Thus the three amido-azobenzenes are related to each other in the following manner :—

AMIDO-AZOBENZENE, or aniline-yellow base,	$C_6H_5.N_2.C_6H_4(NH_2)$
DIAMIDO-AZOBENZENE, or chrysoidine base,	$C_6H_5.N_2.C_6H_3(NH_2)_2$
TRIAMIDO-AZOBENZENE, or phenylene-brown base,	$C_6H_4(NH_2).N_2.C_6H_3(NH_2)_2$

ANILINE YELLOW, $C_6H_5.N_2.C_6H_4.NH_2,HCl$, also called *spirit-yellow*, is the hydrochloride of amido-azobenzene, and can be obtained by mixing dilute aqueous solutions of azobenzene chloride and aniline. In the pure state it forms bluish-violet, lustrous needles, soluble in water with yellow colour turned to a fine red by acids. In strong sulphuric acid it dissolves with brown colour, becoming red on dilution. On heating the aqueous solution of aniline yellow, the free base is precipitated. Free amido-azobenzene is also completely precipitated from its salts by ammonia, and may then be taken up by agitation with ether. In the pure state it forms yellow crystals, which melt at 120° and volatilise unchanged. It is insoluble in water, but soluble in alcohol. Acid solutions dye silk red, the salt itself being taken up, but on washing with water the salt is decomposed and the base imparts a yellow colour to the fibre. Aniline yellow is not fast, and easily volatilises when the fibre is steamed. Hence it is not now used as a dye, but forms the starting point in the manufacture of other aniline colours and of indulines.

CHRYSOÏDINE, $C_6H_5.N_2.C_6H_3(NH_2)_2.HCl$, is the hydrochloride of

dinitrobenzene then thoroughly mixed with the filings, and boiling water added. A violent action occurs, which must be maintained by the gradual addition of another 50 grammes of dinitrobenzene, and the reaction is completed by boiling the liquid for a few minutes. The solution is then made alkaline by adding lime, filtered, and the phenylenediamine extracted from the filtrate by agitation with ether.

Phenylenediamine melts at 63° and boils at 277° C. It is sparingly soluble in water, but very soluble in alcohol and ether. Its solutions are alkaline, and it behaves as a di-acid base, the hydrochloride being $C_6H_4(NH_2)_2,2HCl$.

Ortho- and para-phenylenediamine do not react with diazobenzene compounds.

diamido-azobenzene (page 179). It usually occurs in the form of a reddish-brown crystalline powder, or blackish-green or dark violet crystals having a metallic reflex. It is soluble in boiling water and absolute alcohol. The hot concentrated solution forms a gelatinous blood-red mass on cooling. The brown or orange-coloured aqueous solution is turned red by excess of hydrochloric acid, dyes wool orange-yellow, and gives with alkalies a bright yellow precipitate of the free base, melting at 117°·5 C., and slightly soluble in water, readily in alcohol and ether. Strong sulphuric acid dissolves chrysoïdine with reddish-brown or orange colour, which turns almost scarlet on heating (distinction from phosphine), and cherry-red on dilution. Chrysoïdine is used in combination with safranine to produce a scarlet on mordanted cotton.

PHENYLENE BROWN. $C_6H_4(NH_2).N_2.C_6H_3(NH_2)_2.2HCl$. This colouring matter, which is also known by the name of *Bismarck brown*, *vesuvine*, *Manchester brown*, *cinnamon brown*, *leather brown*, *canelle*, &c., is the hydrochloride of triamido-azobenzene (page 179).[1] The commercial product forms a dark brown powder always containing more or less common salt, and on solution in water often leaves a residue of insoluble impurities. The aqueous and alcoholic solutions are brown, and do not become gelatinous on cooling, but the liquid is turned red by a large excess of hydrochloric acid, though unchanged by slight excess. This reaction is very characteristic. Ammonia and the fixed alkalies give a voluminous brown precipitate of the free base, which is somewhat soluble in boiling water, and more readily in alcohol, and when purified by recrystallisation forms small yellowish-red crystals which melt at 137°. Phenylene-brown dissolves in strong sulphuric acid with reddish-brown coloration, becoming orange-red on dilution. The aqueous solution gives a brown precipitate with basic lead acetate (distinction from chrysoïdine, orange), and is decolorised by treatment with a hydrochloric acid solution of stannous chloride.

Phenylene-brown dyes wool a brownish-orange. It is much used for dyeing leather. On cotton it is mordanted with Turkey-red oil, or by tannin and tartar-emetic.

DIMETHYL-AMIDO-AZOBENZENE, $C_6H_5.N_2.C_6H_4.N(CH_3)_2$, sometimes called *butter yellow*, is the dimethyl-derivative of aniline yellow. When pure, it crystallises in small yellow plates, melting at 115° C., and its hydrochloride forms purple-red hair-like needles. It is insoluble in water, but dissolves with red coloration in hydrochloric acid; and in strong sulphuric acid with yellow colour, turning red on dilution. Its alcoholic solution has been recommended by B. Fischer (*Analyst*, x. 152) as an indicator in alkalimetry, in preference to methyl-orange, which is the ammonium salt of its sulphonic acid (see page 187).

---

[1] Phenylene-brown is prepared on a large scale by reducing a known weight of dinitrobenzene with finely-divided iron and a little hydrochloric acid, and then boiling with water and milk of lime. The solution is filtered from the precipitate of iron oxide, and treated in the cold with the quantity of sodium nitrite and dilute hydrochloric acid requisite to react with the meta-phenylenediamine, when the colour forms immediately, and is salted out and collected on filters.

PHENYL-AMIDO-AZOBENZENE, $C_6H_5.N_2.C_6H_4.NH(C_6H_5)$, is produced by acting on diphenylamine by diazobenzene chloride in alcoholic solution. Its sulphonate is described on page 189. If meta-diazobenzoic acid be substituted for the diazobenzene chloride the product is

PHENYL-AMIDO-AZOBENZOIC ACID, $COOH.C_6H_4.N_2.C_6H_4.NH(C_6H_5)$, which is a yellow colouring matter used under the name of *Jaune solide* or *fast yellow* (for soap). It forms a sparingly soluble brown paste, the solution of which is little changed by alkalies, but changes to a reddish-violet by acids. In strong sulphuric acid it dissolves with violet colour, becoming magenta-red on dilution.

Hydroxy-Azo-Compounds.

When potassium phenate is added to a solution of diazobenzene nitrate, hydroxy-azobenzene is produced according to the following reaction:—

$$C_6H_5.N{:}N.NO_3 + C_6H_5.OK = C_6H_5.N{:}N.C_6H_4.OH + KNO_3.$$

The same body results from the reaction of amido-azobenzene with nitrous acid, or when azobenzene-sulphonic acid is fused with caustic potash. The corresponding derivatives of resorcinol, naphthol, &c., can be obtained by similar means.

HYDROXY-AZOBENZENE, or PHENOL-AZO-BENZENE, $C_6H_5.N_2.C_6H_4.OH$, is best prepared by dissolving 30 parts of potassium nitrite in 4000 parts of water, and adding the solution to 20 parts of phenol and 20 of aniline nitrate dissolved in 2000 parts of cold water. The liquid is filtered after a few hours, and the precipitate treated with ammonia, which leaves resinous matter undissolved. The hydroxy-azobenzene is precipitated from the filtered liquid by hydrochloric acid.

Hydroxy-azobenzene crystallises in yellowish-red rhombic prisms, melting at 152°–154° C. It is only slightly soluble in water, but readily in alcohol. It has marked acid characters, is readily soluble in alkalies, and forms a series of metallic salts. The silver compound is a yellow precipitate which detonates at 100°.

Hydroxy-azobenzene is not employed as a colouring matter, but its sulphonate has been used under the name of *Tropæolin Y* (pages 184, 186).

META-DIHYDROXY-AZOBENZENE, or RESORCINOL-AZO-BENZENE, $C_6H_5.N_2.C_6H_3(OH)_2$. This body is formed by the action of diazobenzene nitrate on an alkaline solution of resorcinol. It forms red needles, melts at 168°, and is readily soluble in alcohol. In commerce it occurs as a brown powder, under the name of *Soudan G.* It is partly soluble in hot water, with yellow colour, the solution giving a bright brown precipitate with hydrochloric acid. In alkalies it is soluble with brown colour, and with concentrated sulphuric acid it yields a yellowish-brown solution, giving a brown precipitate on dilution.

The acid potassium and sodium salts of the sulphonic acid of resorcinol-azobenzene occur in commerce under the name of *Chrysoïn*, *Tropæolin O* or *R*, &c.

BETANAPHTHOL-AZO-BENZENE, $C_6H_5.N_2.C_{10}H_6.OH^{\beta}$. Obtained by the action of diazobenzene nitrate on an alkaline solution of betanaphthol. Under the name of *Soudan I*, it occurs in commerce as a brick-red powder, insoluble in water, but soluble in alcohol with yellow colour. Concentrated sulphuric acid dissolves it with magenta-red colour; and on dilution the solution gives an orange-yellow precipitate.

The sodium salt of the corresponding sulphonic acid forms the colouring matter known as *Crocein orange* or *ponceau 4 BG.*

SOUDAN II is homologous with Soudan I, being produced by the action of a diazoxylene compound on betanaphthol.[1]

ALPHANAPHTHOL-AZO-NAPHTHALENE, $C_{10}H_7.N_2.C_{10}H_6.OH^{\alpha}$, occurs in commerce under the name of *Soudan brown.* It is an insoluble brown powder, dissolving sparingly in dilute alkalies. In concentrated sulphuric acid it dissolves with blue coloration, a brown precipitate being produced on dilution with water.

CARMINAPHTHA is a colouring matter isomeric with Soudan brown, being produced by the reaction of diazotised betanaphthylamine on an alkaline solution of betanaphthol. It is a reddish-brown powder, insoluble in water, but soluble in alcohol. It dissolves in strong sulphuric acid to form a magenta-red solution, which on dilution gives a brownish-red precipitate.

Sulphonated Azo-Compounds.

The amido- and hydroxy-derivatives of azobenzene and its analogues have marked dyeing properties, but owing to their sparing solubility in water it is found convenient to sulphonate them. This is effected by treatment with fuming sulphuric acid; or, instead of sulphonating after diazotising, which lessens the yield of colouring matter, the aniline or other amine is first sulphonated and then diazotised, and the diazo-sulphonic acid formed is then caused to react with other amines or phenols, according to the character of the dye required. In this manner sulphanilic acid, $C_6H_4(SO_3H)^p.NH_2$, and naphthionic acid, $C_{10}H_6(SO_3H)^a.NH_2{}^a$, form the starting points of important series of azo-colouring matters. When diazotised, these two bodies are converted respectively into diazobenzene-sulphonic acid (page 177) and diazonaphthalene-sulphonic acid. By the reaction of the former of these with aniline, *acid yellow* is obtained, while with dimethyl-aniline *helianthin* is the product. With phenol in alkaline solution, the sodium salt of phenyl-diazobenzene-sulphonic acid is obtained, known commercially as *tropæolin Y;* with resorcinol the analagous *chrysoïn* or *tropæolin O* results; alpha-naphthol gives Poirrier's *orange I,* or *tropæolin OOO No. 1;* while betanaphthol yields Poirrier's *orange II* or *mandarin.*

---

[1] Soudan III is the commercial name of a colouring matter of the tetrazo-class.

In the case of the foregoing colours it is always the amine which is sulphonated. On the other hand, if the phenol be first sulphonated, and then caused to react on a diazotised chloride, bodies are obtained which are isomeric with the former, but possess very different colouring and other properties. *Crocein orange* (page 184) is a dye of this class.

Yellow and Orange Sulphonated Azo-Dyes. Tropæolins.

When diazobenzene-sulphonic acid (obtained by mixing solutions of sulphanilic acid and sodium nitrite) acts on amides or alkaline solutions of phenols, a series of colouring matters are obtained, ranging from yellow to deep orange, and called tropæolins, because the shades of colour they produce resemble those of the flowers of *Tropæolum majus.* They usually occur in commerce as sodium salts, and are distinguished according to their shades, tropæolin Y being the most yellow, and then tropæolins O, OO, and so on, as the shade becomes redder.[1] The shade of colour becomes redder by the substitution of toluene, xylene, or cumene for benzene, and hence some of the higher homologues are considered in the section on "azo-reds" (page 191).

The following is a list of the yellow and orange dyes of this class of commercial importance:—

---

[1] A valuable paper by O. Mühlhäuser, on the manufacture of the orange azo-dyes, will be found in the *Jour. Soc. Dyers and Colorists,* iii. 135.

Commercial Name.	Chemical Name or Nature.	Formula.	Remarks.
Amido-Azo-Dyes.			
Acid yellow; Fast yellow. (Page 187.)	K or Na salt of Amido-azobenzene-sulphonic acid (and disulphonic acid). Sulphonated aniline yellow.	$C_6H_4(SO_3Na).N:N.C_6H_4.NH_2.$	...
Helianthin; Methyl orange; Poirrier's orange III. (Page 188.)	Am or Na salt of Dimethylamido-azobenzene sulphonic acid.	$C_6H_4(SO_3Na).N:N.C_6H_4.N(CH_3)_2.$	...
Diphenylamine yellow; Orange IV; Tropæolin OO. (Page 189.)	K or Na salt of Diphenylamine-azobenzene-para-sulphonic acid.	$C_6H_4(SO_3K)^{(4)}.N:N.C_6H_4.NH(C_6H_5).$	...
Metanil yellow; Orange MN. (Page 190.)	Na salt of Diphenyl-amine-azobenzene-meta-sulphonic acid.	$C_6H_4(SO_3Na)^{(3)}.N:N.C_6H_4NH(C_6H_5).$	...
Brilliant yellow; Acid yellow OO; Orange N. (Page 190.)	Na salt of Diphenyl-amine-azo-toluene-sulphonic acid.	$C_6H_3(CH_3)(SO_3Na).N:N.C_6H_4NH(C_6H_5).$	Two isomers occur.
Azoflavine; Azo-yellow. (Page 190.)	A mixture of Nitro-derivatives of di-phenylamine.	...	...
Hydroxy-Azo-Dyes.			
Tropæolin Y. (Page 188.)	Na salt of Phenol-azo-benzene-para-sulphonic acid.	$C_6H_4(SO_3Na)^{(4)}.N:N.C_6H_4.(OH)^{(4)}.$	Nearly obsolete.
Tropæolin R or O; Resorcin yellow; Chrysoïn; Chryseolin. YellowT.	Na salt of Resorcinol-azobenzene-para-sulphonic acid.	$C_6H_4(SO_3Na)^{(4)}.N:N.C_6H_3.\left\{\begin{matrix}OH^{(2)}\\OH^{(4)}\end{matrix}\right.$	Seldom met with.
Tropæolin OOO No. 2;[1] Orange II. β-Naphthol orange. Mandarin G. (P. 188.)	Na salt of Betanaphthol-azobenzene-para-sulphonic acid	$C_6H_4(SO_3Na)^{(4)}.N:N.{}^{a}C_{10}H_6(OH)^{\beta}.$	...
Croceïn orange.[2] (Page 188.)	Na salt of Benzene-azo-betanaphthol-sulphonic acid.	$C_6H_5.N:N.aC_{10}H_5\left\{\begin{matrix}SO_3Na\,a\\OH\beta\end{matrix}\right.$	...
Orange G;[3] Orange yellow. (Page 188.)	Na salt of Benzene-azo-betanaphthol-disulphonic acid.	$C_6H_5.N:N.C_{10}H_4\left\{\begin{matrix}(SO_3Na)_2\\OH^{\beta}.\end{matrix}\right.$	Homologues are red.
Orange No. 3 (not Helianthin). (Page 188.)	Na salt of Meta-nitro-benzene-azo-beta-naphthol-disulphonic acid.	$C_6H_4(NO_2)^{(3)}.N:N.C_{10}H_4\left\{\begin{matrix}(SO_3Na)_2\\HO^{\beta}.\end{matrix}\right.$	Not often met with.

---

[1] *Orange I*, or *Tropæolin OOO No. 1*, the corresponding dye from α–naphthol, is obsolete. *Orange R*, or mandarin G R, and *Orange 2 R*, are homologues of Orange II, being derived from toluidine and xylidine respectively, instead of from aniline.

[2] *Tropæolin OOOO*, the corresponding dye from α-naphthol, is obsolete. *Orange GT* and *Scarlet GR* are homologues prepared respectively from toluidine and xylidine instead of aniline.

[3] *Ponceau 2 G* is isomeric with Orange G, and *Ponceau G T* and *R T* are homologues from toluidine. (See also page 192.)

The following table shows the general character and reaction of more important orange and yellow sulphonated azo-dyes :—

Commercial Name of Dye.	Characters of Solid Dye of Commerce.	Colour of Aqueous Solution.	Behaviour of Aqueous Solution with Reagents.				Reaction of Solid Dye with Sulphuric Acid.		Products formed on Reduction with Zinc and Hydrochloric Acid (see page 211).
			On adding Caustic Soda.	On adding Hydrochloric Acid.	With Barium Chloride.	With Calcium Chloride.	With Strong Acid.	On Dilution with Water.	
AMIDO-AZO-DYES.									
Acid yellow.	Yellow powder.	Yellow.	No change.	Yellow ppte. soluble in excess with reddish-yellow or cherry-red colour.	Precipitate.	No precipitate.	Brownish-yellow.	Orange-yellow.	Sulphanilic acid and para-diamido-benzene.
Helianthin; Methyl orange.	Orange-yellow powder.	Orange.	No change; orange ppte.	Red-violet; crystalline ppte. in strong solution.	...	...	Yellow or reddish-brown.	Carmine-red.	Sulphanilic acid and dimethyl-para-diamido-benzene.
Diphenylamine yellow.	Orange-yellow crystalline powder.	Yellow.	No change.	Red colour; or violet precipitate.	Precipitate.	Precipitate.	Violet.	Reddish-violet with slate grey precipitate.	Sulphanilic acid and para-amido-diphenylamine.
Metanil yellow.	Brownish-yellow powder.	Orange.	No change.	Precipitate and crimson-red colour.	Sparingly soluble ppte.	Sparingly soluble ppte.	Dirty violet.	Magenta-red.	Amidobenzene-meta-sulphonic acid and para-amido-diphenylamine.
Orange N.	Orange-red sparingly soluble.	Yellow.	Yellow ppte.	Violet or steel-blue ppte.	Yellow crystalline ppte.	...	Bluish-green.	Violet with steel blue ppte.	...
Azoflavine.	Ochre-yellow powder.	Yellow.	Yellow-brown colour.	Reddish-violet or brownish.	Sparingly soluble crystalline ppte.	No precipitate.	Reddish-violet.	Red and brown yellow ppte.	...

Commercial Name of Dye.	Characters of Solid Dye of Commerce.	Colour of Aqueous Solution.	Behaviour of Aqueous Solution with Reagents.				Reaction of Solid Dye with Sulphuric Acid.		Products formed on Reduction with Zinc and Hydrochloric Acid (see page 211).
			On adding Caustic Soda.	On adding Hydrochloric Acid.	With Barium Chloride.	With Calcium Chloride.	With Strong Acid.	On Dilution with Water.	
HYDROXY-AZO-DYES.									
Tropæolin Y.	Brownish-yellow powder.	Reddish-yellow.	No change.	No change.	...	...	Brownish-yellow.	No change.	Sulphanilic acid and amido-phenol.
Resorcin yellow; Chrysoïn.	Brown powder.	Orange.	Reddish-brown.	No change.	...	...	Orange-yellow.	Reddish-yellow.	Sulphanilic acid and amido-resorcinol.
Orange I; α-Naphthol yellow.	Brick-red powder.	Orange.	Red-brown.	Yellow-brown flakes.	...	Red precipitate.	Violet.	Brown precipitate; followed by orange solution.	Sulphanilic acid and amido-alphanaphthol.
Orange II; β-Napthol yellow; Mandarin.	Yellow-red powder.	Orange.	Changed to brown-red.	Brownish-yellow ppte. in strong solutions only.	Sparingly soluble crystalline precipitate.	Yellow ppte., becoming dirty red and crystalline on boiling with water.	Carmine-red.	Brownish-yellow precipitate.;	Sulphanilic acid and amido-betanaphthol.
Crocein. orange.	...	...	...	Yellow-brown precipitate.	...	...	Orange-yellow.	Yellow-brown precipitate.	Aniline, amido-betanaphthol, and sulphuric acid.
Orange G.	Yellowish-red powder.	Orange-yellow.	Changed to brown.	Not changed.	...	Orange scales.	Orange-yellow.	Unchanged.	Aniline, amido-betanaphthol, and sulphuric acid.
Orange No. 3 (not Helianthin).	Red-brown powder.	Reddish-yellow.	Changed to yellowish-brown.	Orange-yellow precipitate, soluble in much water.	...	...	Orange-yellow.	Orange ppte.; soluble in excess of water to a yellow solution.	Nitraniline, amido-betanaphthol, and sulphuric acid.

The best way of effecting the reduction of the yellow or orange azo-dyes is to warm the solution of the colouring matter with zinc-dust and hydrochloric acid, the action in an ammoniacal solution being somewhat slow. Reduction with ammonium sulphide, in the manner described on page 211, may sometimes be conveniently employed.

The following is a detailed description of some of the more important sulphonated azo-yellows and oranges:—

Acid Yellow. Fast Yellow.[1] (See page 184.) When aniline is heated with fuming sulphuric acid, para-amidobenzene-sulphonic acid (sulphanilic acid) is obtained. On dissolving this in a large quantity of water and adding sodium nitrite and hydrochloric acid, diazobenzene-sulphonic acid results. On treating the solution with aniline, removing the excess of the latter by hydrochloric acid, and adding common salt, the amido-azo-benzene-sulphonic acid, $C_6H_4(SO_3H).N_2.C_6H_4(NH_2)$, separates as a yellow precipitate, and forms the *solid yellow S* of commerce.[2] It is also prepared by heating aniline yellow with from three to four parts of fuming sulphuric acid. The commercial product known as *acid yellow* is prepared by dissolving the sulphonic acid in sodium carbonate and precipitating the solution by common salt. The potassium salt is also employed. Acid yellow is a yellow powder, readily forming a yellow solution in water, but only sparingly soluble in alcohol. On acidulating the aqueous solution with hydrochloric acid the free sulphonic acid is thrown down in the form of minute needles, soluble in excess of hydrochloric acid with reddish-yellow colour, appearing crimson in thin layers, the change being probably due to the formation of a hydrochloride. Acid yellow is not precipitated by ammonia or fixed alkalies, nor by basic lead acetate. It is precipitated by barium chloride, but not by calcium chloride. Sulphuric acid dissolves the solid dye with yellow colour. Zinc-dust decolorises the solution, but the filtered liquid recovers its yellow colour on exposure to the air.

Acid yellow is used as a yellow dye for wool and silk, and is also employed for the manufacture of *Biebrich scarlet* (page 197).

---

[1] *Acid yellow G* (gelb) is a derivative of amido-azobenzene. The homologue from amido-azotoluene is somewhat more orange in shade, and is known as *acid yellow R*, or *fast yellow R*. The name *fast yellow* is also applied to diphenylamine yellow and to a body of the formula, $C_6H_4(COOH).N_2.C_6H_4.NH(C_6H_5)$ (see page 181).

[2] Much of the acid yellow of commerce contains more or less of a disulphonate.

HELIANTHIN. METHYL ORANGE. Poirrier's Tropæolin D. Orange III.[1] Gold-orange. Mandarin Orange (page 184). These names, among others, are applied to the ammonium or sodium salt of dimethyl-amido-azobenzene-sulphonic acid, or parasulphobenzene-azodimethylaniline, $C_6H_4(SO_3H)^{(4)}.N_2{}^{(1)}.C_6H_4.N(CH_3)_2{}^{(4)}$, a body produced by the action of dimethyl-aniline on diazobenzene-sulphonic acid. Helianthin forms an orange-yellow powder, readily soluble in hot water, but only sparingly in alcohol. The aqueous solution is orange-yellow, and is not precipitated by alkalies. On adding hydrochloric acid to a hot, concentrated aqueous solution, the free sulphonic acid is precipitated in microscopic needles, which soon change to small, strongly lustrous plates or prisms having a violet reflection. Concentrated sulphuric acid dissolves helianthin with reddish or yellowish-brown colour, the solution appearing yellow in thin layers. On copious dilution, the liquid becomes a splendid red. With most reagents, helianthin behaves similarly to acid yellow, but basic acetate of lead throws down the whole of the colouring matter as an orange-yellow precipitate. Sodium chloride or magnesium sulphate added to a dilute solution of helianthin precipitates the colouring matter in microscopic crystals.

Silk and wool when immersed in an acid solution of helianthin are dyed a fiery orange. The dyed fibre is turned red by hydrochloric acid, and yellow by strong sulphuric acid, but alkalies produce no change.

Methyl-orange now receives extensive application as an indicator in alkalimetry. The yellow colour which it imparts to aqueous and alcoholic liquids is changed to red by a strong acid, but is wholly unaffected by weak acids. Thus the titration of sodium carbonate by sulphuric or hydrochloric acid can be effected in the cold, if helianthin be used as the indicator of neutrality, the carbonic acid liberated having no effect on the colouring matter.[2]

The following acids are wholly unindicated by methyl-orange, and hence the base of their salts can be titrated by hydrochloric acid in the cold just as though the acids were absent:—carbonic, hydrocyanic, hydrosulphuric, arsenious, silicic, boric, oleic, stearic, palmitic, carbolic, &c. With oxalic, acetic, butyric, succinic, lactic, tartaric, and citric acids inaccurate results are obtained, but sulphuric, hydrochloric, and nitric acids give sharp end-reactions. The following salts are neutral to methyl-orange, and hence their formation is an end-point of titrations in which they are produced:— $Na_2S_2O_3$, $KaHSO_3$, NaH_2PO_4, $CaH_4(PO_4)_2$, NaH_2AsO_4, $K_2Cr_2O_7$. Methyl-orange can be used to detect free acid in alum, ferrous sulphate, cupric chloride, &c. The earthy carbonates in hard water (which occasion the so-called "temporary hardness") may be at once determined by titrating the water with a mineral acid and methyl-orange.

---

[1] *Orange III* is a name which is also applied to a colouring matter patented by Roussin and Poirrier, and having the constitution of a sodium salt of metanitrobenzene-azobetanaphthol-disulphonic acid (see page 184).

[2] The delicacy and applications of methyl-orange and other indicators in volumetric analysis have been described in a series of valuable papers by R. T. Thompson (*Jour. Soc. Chem. Ind.*).

Ethyl-orange is preferred by Wieland to its lower homologue as an indicator of neutrality. Lacmoïd, cochineal, congo-red, and dimethyl-amidoazobenzene behave much like helianthin.

Methyl-orange is not applicable as an indicator in presence of nitrous acid or nitrites, which compounds decompose it.

DIPHENYLAMINE YELLOW (pages 184, 185). This colouring matter, the *Tropæolin OO*[1] of M. Witt, and Poirrier's *orange MN*, also known as *gold-orange*, *acid-yellow D*, *diphenylamine-orange*, *fast-yellow*, and *Manchester-yellow* (Perkin), is a phenylated acid yellow. The free sulphonic acid is obtained by the action of diazobenzene-sulphonic acid on diphenylamine. The diphenylamine is added in the form of powder to the solution of the diazobenzene sulphonic acid (diazotised sulphanilic acid) and the mixture agitated for some hours, till the reaction is complete. It forms steel-grey needles, very sparingly soluble in water with pink coloration. It is a powerful acid, forming well-defined salts, almost all of which are remarkable for their insolubility.[2] The commercial dye is a potassium or sodium salt, and forms an orange-yellow crystalline powder, or golden-yellow dichroïc crystals, often arranged in the form of a fan. It is readily soluble in hot water, but only very sparingly in cold water or alcohol. Very small quantities of mineral salts precipitate it from its solutions. The hot aqueous solution is yellow, and unchanged by caustic alkalies, but turned reddish-violet by hydrochloric acid, and on cooling a violet precipitate is formed. Calcium and barium chlorides give yellow crystalline precipitates. In strong sulphuric acid, the dye dissolves with violet colour, becoming redder on adding water, while a slate-grey precipitate is produced.

A nitro-derivative occurs in commerce under the same name. When the solution is reduced with zinc and hydrochloric acid and filtered, the filter-paper is stained brown. The solid substance deflagrates and gives off yellow vapours when heated on platinum foil (see Azoflavine).

[2] The trimethylamine salt is the only one easily soluble in cold water. The aniline salt when treated with an excess of boiling aniline is suddenly transformed into induline, $C_{18}H_{15}N_3$, a blue colouring matter isomeric with phenyl-amido-azobenzene.

When reduced with an acid solution of stannous chloide, tropæolin OO yields sulphanilic acid and para-amido-diphenylamine, which may be extracted by ether after adding excess of caustic soda to the solution.

Diphenylamine yellow gives a fine golden-yellow on silk or wool. The fibre is turned blue-violet by sulphuric and red-violet by hydrochloric acid.

Tropæolin OO may be substituted for methyl-orange as an indicator in alkalimetry, a faint trace of strong mineral acid turning the dilute solution red, while carbonic and other weak acids have no effect.[1]

Metanil yellow is isomeric with diphenylamine yellow. *Brilliant yellow, acid yellow OO, yellow N,* and *orange N* are names given to the homologues of diphenylamine yellow. Two distinct isomers are met with (see page 184).

Luteoline is a higher homologue from diazotised metaxylidinesulphonic acid. It is now nearly obsolete, but occurred as a difficultly soluble orange-yellow powder. The hot aqueous solution deposits crystals on cooling, gives an orange-yellow precipitate with soda, and a violet precipitate with hydrochloric acid. In strong sulphuric acid the dye dissolves with yellowish-green colour, a violet precipitate being formed on dilution. With calcium chloride, luteoline gives an orange precipitate, which on boiling becomes red and crystalline.

AZOFLAVINE is produced by the nitration of diphenylamine yellow, and is a mixture of more or less mono-, di- and tri-nitrodiphenylamine with the body $C_6H_4(SO_3H_2).N_2.C_6H_4.NH(C_6H_4NO_2)$. It forms an ochre-yellow powder, soluble with difficulty in cold but readily in hot water. The aqueous solution is yellow, changing to brownish on addition of hydrochloric acid. When reduced in ammoniacal solution it becomes yellow. Barium chloride gives a slightly soluble crystalline precipitate, but no change results with calcium chloride. The solid dye dissolves in strong sulphuric acid with magenta-red colour, changing to yellowish-red, with a yellowish-brown precipitate, on dilution with water. When heated on platinum foil the dye forms "Pharoah's serpents," and gives off yellow vapours. After reduction and filtration, brown spots are produced on the filter paper.

Curcumeïn, Azoflavine S or *2, Azo-yellow, Citronine B* or *2 B, Indian Yellow,* and *New yellow,* are names applied to varieties of azoflavine. They must not be confounded with the *citronin* of

---

[1] Tropæolin OOO, or naphthol-azobenzene-sulphonic acid, behaves in a precisely opposite manner, being turned red by a trace of alkali.

Brooke, Simpson, and Spiller (page 156), or with *curcumin S* or *sun-yellow*, which is the sodium salt of azo-oxystilbene-disulphonic acid.

Azo-Reds.

The scarlets, ponceaus, and clarets derived from azobenzene and its allies are among the most important of the colouring matters from coal-tar. The ready production and fast character of crocein scarlet and allied dyes seem not unlikely to cause the extinction of the cochineal industry. The general method of producing the azo-reds may be exemplified by the process of preparing *xylidine-red*. For this purpose, xylidine, $C_6H_3(CH_3)_2NH_2$, is dissolved in twice the quantity of hydrochloric acid necessary to combine with it, and after copious dilution of the liquid with ice-cold water a solution of the calculated quantity of sodium nitrite is gradually added with constant stirring. The resultant (neutral) solution of diazoxylene chloride is allowed to flow into a dilute ammoniacal solution of sodium betanaphtholdisulphonate, when ammonium chloride and *xylidine-scarlet* or sodium xylene-azobeta-naphthol-alpha-disulphonate are produced:—

$$C_6H_3(CH_3)_2.N_2.Cl + C_{10}H_5(SO_3Na)_2.OH^{\beta} + NH_3$$
$$= NH_4Cl + C_6H_3(CH_3)_2.N_2.C_{10}H_4(SO_3Na)_2.OH^{\beta}.$$

After standing, the liquid is boiled, filtered from resinous matter, and the colouring matter precipitated by addition of salt.[1]

The following table contains a description of some of the more important azo-dyes of which xylidine scarlet is the type. The list is by no means a complete one, and new colouring matters of the same class are being continually produced. The commercial names of the dyes are often confusing, the same chemical compound receiving different names from its several makers, while on the other hand identical or very similar names are commercially used to distinguish dyes of distinctly different chemical nature.

---

[1] Owing to the facility with which diazo-compounds react with phenoloids and their sulphonic acids in alkaline solution, it is possible to produce azo-dyes directly on the fibre by immersing the goods alternately or simultaneously in a solution of naphthol and the diazo salt, and then developing the colour in an alkaline bath. The method is especially applicable to cotton, which does not take up ready-formed azo-dyes. Another method of operating is to employ the nitrite required for diazotising in the form of an ammonium salt, when on heating the goods this is decomposed in the presence of the phenoloid and amine, and thus produces the azo-colour *in situ*. The colouring matter known as *primuline* can be diazotised in the fabric, and on subsequently immersing the goods in an alkaline solution of resorcinol or naphthol the azo-dye is developed (page 209). The property possessed by the hydroxyazo-dyes of forming soluble compounds with acid sulphite of sodium which are decomposed by heat is also utilised. *Narceine*, $C_6H_4(SO_3Na).NH.N(NaSO_3).C_{10}H_6.OH^{\beta}$, is a substance of this class.

Commercial Name.	Formula.	Remarks. (See page 194.)	Characters of Dye.
Archil substitute. Naphthionic Red.	$C_6H_4(NO_2)^o.N^p : N.C_{10}H_5\left\{\begin{matrix}SO_3Na^\alpha\\NH_2^\alpha\end{matrix}\right.$	From naphthionic acid.	Brown paste; red-brown solution.
Cochineal Scarlet 2 R.	$C_6H_4(CH_3).N : N.C_{10}H_5\left\{\begin{matrix}SO_3Na\\OH^\alpha\end{matrix}\right.$	From C acid. Homologue is scarlet 4 R.	Cinnabar-red powder, soluble in hot water to yellow-red solution.
Scarlet G T.	$C_6H_4(CH_3).N ; N.C_{10}H_5\left\{\begin{matrix}SO_3Na\\OH^\beta\end{matrix}\right.$	From S acid. Homologue is scarlet G R.	Scarlet powder; solution orange-yellow.
Azococcin 2 R.	$C_6H_3(CH_3)_2.N ; N.C_{10}H_5\left\{\begin{matrix}SO_3Na\\OH^\alpha\end{matrix}\right.$	From Nevile's acid.	Brown-red powder, difficultly soluble; bronzy crystals on cooling.
Wool Scarlet R.	$C_6H_3(CH_3)_2.N : N.C_{10}H_4\left\{\begin{matrix}(SO_3Na)_2\\OH^\alpha\end{matrix}\right.$	From R Salt.	Brown-red powder; solution yellowish-red.
Ponceau R. Scarlet R. Xylidine Scarlet.	$C_6H_3(CH_3)_2.N : N.C_{10}H_4\left\{\begin{matrix}(SO_3Na)_2\\OH^\beta\end{matrix}\right.$	From R Salt. Isomers of yellower shade from G salt. Ponceau G, and scarlet G.	Scarlet powder; easily soluble; red solution.
Ponceau 2 G and 2 R. Scarlet 2 G and 2 R.	$C_6H(CH_3)_2(CH_3)_2.N : N.C_{10}H_4\left\{\begin{matrix}(SO_3Na)_2\\OH^\beta\end{matrix}\right.$	From G salt. Isomers from R salt.	Brown-red powder. Fine red solution.
Ponceau 3 R.	$C_6H_2(CH_3)_2(C_2H_5).N : N.C_{10}H_4\left\{\begin{matrix}(SO_3Na)_2\\OH^\beta\end{matrix}\right.$	From R salt.	Dark red powder; solution cherry-red.
Anisol Red. Anisidine Ponceau.	$C_6H_4(OCH_3).N : N.C_{10}H_4\left\{\begin{matrix}(SO_3Na)_2\\OH^\beta\end{matrix}\right.$	From R salt.	Brownish-red powder; solution cherry-red.
Phenatol Red. Coccinin. Coccin.	$C_6H_4(OC_2H_5).N : N.C_{10}H_4\left\{\begin{matrix}(SO_3Na)_2\\OH^\beta\end{matrix}\right.$	From R salt.	Fine red solution.
Coccinin B.	$C_6H_3(CH_3)^1(OCH_3)^p.N : N.C_{10}H_4\left\{\begin{matrix}(SO_3Na)_2\\OH^\beta\end{matrix}\right.$	From R salt.	Dark red powder; solution cherry-red.
Bordeaux G. Claret G.	$C_{10}H_7.N^\alpha : N^\alpha.C_{10}H_4\left\{\begin{matrix}(SO_3Na)_2\\OH^\beta\end{matrix}\right.$	From G salt. Bluer shades from R salt.	Solution claret coloured.
Crystal Ponceau 6 R.	Isomeric with Bordeaux G.	From γ acid.	Red-brown glittering crystals; solution deep red.
Fast Brown N; Acid Brown; Napthylamine Brown.	$C_{10}H_6(SO_3Na)^\alpha. N^\alpha : N^\alpha.C_{10}H_6.OH^\alpha$	From naphthionic acid.	Dark brown powder; solution reddish-brown.
Roccelline. Fast Red A. Rubidine. Cerasine.	$C_{10}H_6(SO_3Na)^\alpha.N^\alpha : N^\alpha.C_{10}H_6.OH^\beta$	From naphthionic acid.	Solution reddish-brown, forms brown jelly when rapidly cooled.
Fast Red C. Azorubin S. Carmoisin.	$C_{10}H_6(SO_3Na)^\alpha.N ; N.C_{10}H_5\left\{\begin{matrix}SO_3Na^\alpha\\OH^\alpha\end{matrix}\right.$	From naphthionic acid and Nevile's acid.	Brown powder; magenta-red solution.
Crocein Scarlet 7 B extra.	$C_{10}H_6(SO_3Na)^\alpha.N : N.C_{10}H_5\left\{\begin{matrix}SO_3Na^\alpha\\OH^\beta\end{matrix}\right.$	From naphthionic and B acids.	...
New Coccin. Brilliant Ponceau.	$C_{10}H_6(SO_3Na)^\alpha.N^\alpha : N^\alpha.C_{10}H_4\left\{\begin{matrix}(SO_3Na)_2\\OH^\beta\end{matrix}\right.$	From naphthionic acid and G salt.	Scarlet-red powder; sparingly soluble.
Fast Red D. Amaranth.	$C_{10}H_6(SO_3Na)^\alpha.N : N.C_{10}H_4\left\{\begin{matrix}(SO_3Na)_2\\OH^\beta\end{matrix}\right.$	From naphthionic acid and R salt.	Reddish-brown powder; solution magenta-red.

Reaction of Aqueous Solution.		Reaction of Dye with Sulphuric Acid.		Products of Reduction with Zinc of Ammonia.	Other Characters.
With Caustic Soda.	With Hydrochloric Acid.	With Strong Acid.	On Dilution with Water.		
Precipitate soluble in water.	Precipitate.	Magenta-red.	Brown-red ppte.	Nitraniline and diamidonaphthalene sulphonic acid.	...
Orange coloration.	Red flakes.	Magenta-red.	Red flakes.	Toluidine and amido-α-naphthol sulphonic acid.	...
Brown-red coloration.	Brown oily drops.	Magenta-red.	Oily drops.	Toluidine and amido-β-naphthol sulphonic acid.	...
Brown-yellow colour; no ppte.	Brownish-red flakes.	Magenta-red.	Brown-red precipitate.	Xylidine and amido-α-naphthol sulphonic acid.	...
Yellow-red colour.	Bluish-red coloration.	Cherry-red.	Red solution.	Xylidine and amido-α-naphthol disulphonic acid.	...
No precipitate.	No change.	Red.	Brown precipitate.	Amido-β-naphthol disulphonic acid and xylidine.	$BaCl_2$ and $CaCl_2$, amorphous precipitates.
No change.	No change.	Eosin-red.	Yellow-red colour.	Amido-β-naphthol disulphonic acid and cumidine.	$BaCl_2$ and $CaCl_2$, precipitates appearing slowly.
Yellow precipitate.	No change.	Cherry-red.	Cherry-red.	Amido-β-naphthol disulphonic acid and ethyl-xylidine.	...
Yellowish-red.	No change.	Magenta-red.	Cherry-red.	Amido-β-naphthol disulphonic acid and anisidine.	...
Brownish coloration.	...	Magenta-red.	Red.	Amido-β-naphthol disulphonic acid and phenatidine.	$BaCl_2$, brown, sparingly soluble precipitate. $CaCl_2$ red precipitate gradually.
Brown ppt. soluble to red-brown solution.	Darkened.	Magenta- or cherry-red.	Cherry-red.	Amido-β-naphthol disulphonic acid and methyl anisidine.	$BaCl_2$, brown ppte. $CaCl_2$, red precipitate formed gradually.
Brown.	Darkened.	Indigo blue.	...	Amido-β-naphthol disulphonic acid and α-naphthylamine.	$BaCl_2$, flocculent precipitate. $CaCl_2$ only precipitates strong solutions.
Bright brown.	Darkened; with excess, brown crystalline ppt.	Violet.	Scarlet.	...	...
No change.	Brown ppte.	Blue.	Brown ppt.	Amido-α-naphthol and α-naphthol-amine sulphonic acid.	...
Darkened.	Yellow-brown ppte.	Violet.	Yellow-brown ppte.	Amido-α-naphthalene sulphonic acid, and amido-β-naphthol.	Na_2CO_3 in strong solution gives pale brown crystals.
Becomes yellow.	Brown jelly.	Bluish-violet.	Magenta-red.	α-naphthylamine sulphonic acid and amido-α-naphthol sulphonic acid.	$CaCl_2$, red crystalline precipitate.
...	...	Violet.	Red.	α-naphthylamine sulphonic acid and amido-β-naphthol sulphonic acid.	$MgSO_4$ gives crystalline ppte. in strong solutions.
Brown.	No change.	Magenta-red.	Yellow-red.	α-naphthylamine sulphonic acid and amido-β-naphthol disulphonic acid.	...
Becomes dark.	No change.	Violet.	Magenta-red.	...	...

The dyes of the class of which xylidine scarlet is the type are very numerous, and are being continually added to. The characters of the dyes are materially dependent on their derivation from alpha- or beta-naphthol, and the exact nature of the isomeric naphthol-sulphonic acids employed also notably affect the colour and other properties of the dye. The letters R and G (the initial letters of the words *roth* and *gelb*), appended to the commercial names of the scarlets and other azo-dyes, have reference to the sodium salts of the respective isomeric beta-naphtholdisulphonic acids used for their production. "Salt G" yields the yellow shades, and "salt R" the red shades of the azo-dyes they are employed to produce. Similarly, where beta-naphtholmonosulphonic acid is used, the characters of the resultant dyes depend to some extent on the isomer employed, whether "Schäffer's acid," "Bayer's acid," or other modification.[1]

---

[1] When betanaphthol is heated with twice its weight of strong sulphuric acid (sp. gr. 1·845) to about 90° C., until completely sulphonated, the chief product is a monosulphonic acid known as Schäffer's acid ("acid S"). When betanaphthol is added gradually to twice its weight of strong sulphuric acid (sp. gr. 1·845), taking care that the temperature does not rise above 50° to 60° C., Schäffer's acid and an isomeric acid, betanaphthol-alphasulphonic acid, often known as Bayer's acid ("acid B"), are formed in about equal quantity. The use of a temperature of 20° C. for preparing Bayer's acid has been patented. Schäffer's and Bayer's acids may be separated by converting them into sodium salts and treating the dry product with alcohol, in which liquid the salt of betanaphthol-alphasulphonic acid is by far the most readily soluble. Another method of separating Bayer's acid from Schäffer's and another isomeric said to be present is based on the different facility with which the three acids act on certain azo-compounds. Thus by treating the alkaline solution of the mixed sulphonic acids with a properly regulated quantity of tetrazo-diphenyl, the unnamed acid and Schäffer's acid are precipitated as claret-coloured dyes, while Bayer's acid remains in solution in the requisite purity for the manufacture of croceïn scarlet, for which purpose the isomeric acids are not available. A naphthol-sulphonic acid distinct from, and giving shades redder than, either the above acids, is said to be obtainable by a process described in Patent No. 15,781, of 1885 (*Jour. Soc. Dyers, &c.*, ii. 199).

When betanaphthol is heated with three times its weight of concentrated sulphuric acid (1·845 sp. gr.) to 100° or 110° C., it is converted into a mixture of two isomeric disulphonic acids. To separate these, the liquid should be diluted, neutralised with milk of lime, and filtered after allowing sufficient time for the precipitated calcium sulphate to crystallise. The filtrate is treated with sodium carbonate, and the filtered liquid evaporated to dryness. From the mixture of the isomeric sodium salts obtained, "salt G" can be dissolved by alcohol, while "salt R" is left insoluble. According to J. Wetter (*Jour. Soc. Chem. Ind.*, iv. 339), the isomeric acids can be separated by treating the solution of their *acid* sodium salts with brine, when salt R

Xylidine Red, or Scarlet R, obtained as described on page 191, forms a scarlet-red powder, readily soluble in water or acetic acid, but less so in glycerin or alcohol. Its aqueous solution is unchanged by alkalies or dilute acids, and gives scarlet lakes with the acetates of lead and aluminium. Barium chloride precipitates it more perfectly, even in the presence of acetic acid. Xylidine scarlet dyes animal fibres without a mordant in a slightly acid bath. When fixed by means of a barium salt, it withstands the action of boiling water very well. The colour does not stand soaping, but is fast in the air, and resists the action of light fairly well, though it fades slowly when exposed to direct sunshine.

Xylidine red and allied colours are frequently adulterated with *dextrin*, which may be separated by treating the sample with sufficient alcohol. Tarry matters are sometimes precipitated on acidulating the solution of the dye with acetic acid.

Fast-Brown N. By the action of alphanaphthol on diazotised naphthionic acid a compound is obtained having a naphthalene nucleus on both sides of the chain, and of the following formula:—$C_{10}H_6(SO_3Na)^{\alpha}.N_2.C_{10}H_6(OH)^{\alpha}$. This colouring matter, like others of similar constitution, dyes wool brown in an acid bath. It forms a dark brown powder soluble in water to form a yellowish-brown solution, changed to brownish-red by soda and giving a brown precipitate with hydrochloric acid. In strong sulphuric acid the dye dissolves with blue colour, a brown precipitate being formed on dilution.

An isomeric colouring matter from alphanaphthol and diazotised beta-naphthylamine-sulphonic acid gives a brownish-red solution, turned magenta-red by soda or dilute acids. It is soluble in strong sulphuric acid with blue colour, giving a reddish-violet precipitate on dilution.

Other brown colouring matters are described with the tetrazo-dyes (page 199).

crystallises out, while salt G remains in solution. (The same process is said to be applicable to the separation of Schäffer's and Bayer's monosulphonic acids.) Another betanaphthol-disulphonic acid (γ) has been described and patented by Gans and Hoffman (*Jour. Soc. Chem. Ind.*, iii. 567; iv. 742), and is used for the production of *crystal ponceau 6 R*, by reaction in alkaline solution with diazotised α-naphthylamine.

By the extreme action of fuming sulphuric acid on betanaphthol, a trisulphonic acid is obtainable.

The manufacture of sulphonic acids and nitrosulphonic acids from alphanaphthol has been recently patented by H. Caro. Other sulphonic acids of alpha- and beta-naphthol and of the naphthylamines have been described and patented.

Secondary Azo-Compounds. Tetrazo-Dyes.

Amido-azobenzene may be regarded as a primary amine, since it contains the group NH_2. When this is attacked by nitrous acid the diazo-reaction occurs, and a diazo-azobenzene compound is formed: — $C_6H_5.N_2.C_6H_4NH_2HCl + NaNO_2 + HCl = C_6H_5.N_2.C_6H_4.N_2.Cl + NaCl + 2H_2O$. The product contains the —N : N— group in two places, and is called a secondary azo- or tetrazo-compound.[1] By reaction with phenols in presence of alkalies, these tetrazo-compounds yield products of which several have received practical applications, as they usually possess a colouring power superior to that of the azo-dyes of similar colour but simpler constitution. They are rendered soluble by sulphonation, the SO_3H group being often introduced into both chains. Thus by diazotising acid yellow, and acting with the product on sodium betanaphthol-alphasulphonate (Bayer's salt), sodium betanaphtholsulphonate-azobenzene-azobenzene-sulphonate of ammonium, or *croceïn scarlet*, is obtained, according to the following equation:—

$$C_6H_4(SO_3H).N:N.C_6H_4.N:N.Cl + C_{10}H_6(SO_3Na)^{\alpha}.OH^{\beta} + 3NH_3 =$$
$$NH_4Cl + C_6H_4(SO_3.NH_4)^{p}.N^{1}:N^{p}.C_6H_4.N^{1}:N^{\alpha}.C_6H_5(SO_3Na).OH^{\beta}.$$

CROCEÏN SCARLET 3 B, or *Ponceau 4 RB*, formulated above, is a dye of considerable practical importance. It forms a red-brown powder, soluble in water with scarlet-red colour. The solution is turned violet-red by alkalies, but not precipitated except in very concentrated solutions. With hydrochloric acid it yields a yellowish-brown precipitate. With barium chloride it gives a red precipitate, becoming dark violet and crystalline on boiling. With calcium chloride the dye gives a flocculent red precipitate, which on boiling the liquid suddenly becomes brown and crystalline. When reduced with zinc in ammoniacal solution croceïn scarlet is decolorised, but the liquid acquires a yellow colour on exposure to air. The solid dye dissolves in strong sulphuric acid with indigo-blue colour, and on dilution a yellow-brown precipitate is formed, soluble in more water to a red solution.

CROCEÏN SCARLET 7 B, or *Ponceau 6 RB*, is homologous with the last (containing two toluene- instead of benzene-residues) and resembles it generally, but after reduction with zinc and ammonia the colourless liquid does not again become yellow on exposure to air. The hot concentrated aqueous solution, when treated with magnesium sulphate and allowed to stand, deposits on cooling long silky needles of the magnesium salt.

---

[1] *Tertiary Azo-Compounds*, containing three —N : N— groups, have been prepared (R. Meldola, *Jour. Chem. Soc.*, xliii. 486), but they have little tinctorial value.

PONCEAU S. EXTRA is a disulphonated croceïn scarlet:—$C_6H_4(SO_3Na).N_2.C_6H_3(SO_3Na).N_2.C_{10}H_4(SO_3Na)_2.OH^\beta$.

Orseillin 2 B is the metameric compound from alphanaphthol sulphonic acid.

BIEBRICH SCARLET, *Ponceau 3 R*, or *azobenzene red*, is a mixture of *fast scarlet or double scarlet*, $C_6H_4(SO_3Na).N_2.C_6H_4.N_2.C_{10}H_6.OH^\beta$, with the corresponding disulphonate, $C_6H_4(SO_3Na)^p.N^1:N^p.C_6H_3(SO_3Na)^o.N^1:N^\alpha.C_{10}H_6.OH^\beta$. It is a reddish-brown crystalline powder, forming a yellowish-red solution. The hot aqueous solution of Biebrich scarlet becomes gelatinous on cooling. Dilute acids give a flocculent brownish-red precipitate in strong solutions, but the dye is not precipitated by alkalies. (According to some, a brownish-red precipitate.) With zinc and ammonia the solution of Biebrich scarlet is decolorised, but on exposure to air the liquid becomes yellow and gives the reactions of acid yellow. The solid dye gives a green solution in strong sulphuric acid, and on adding water the colour changes to blue, then to violet, and lastly a dirty-brown precipitate is formed.

Scarlets 3 B, 3 R, and 4 R are varieties of Biebrich scarlet.

SCARLET S, or *Ponceau SS extra*, is metameric with Biebrich scarlet, the betanaphthol being sulphonated instead of the amine, thus:—$C_6H_5.N:N^p.C_6H_4.N^1:N.C_{10}H_4(SO_3Na)^\alpha{}_2.OH^\beta$, or azobenzene-azobenzene-betanaphthol-disulphonate of sodium. It is a brown powder, soluble in water with magenta-red colour. The solution yields a violet precipitate with hydrochloric acid, and is turned reddish-violet by soda.

Brilliant croceïn M is a dye of the same composition prepared with sodium betanaphthol-γ-sulphonic acid instead of salt R. It is a light brown powder, forming a cherry-red solution, which is turned brown by soda, and gives a brown precipitate with hydrochloric acid.

Azococcin 7 B and Croceïn B are colouring matters from alphanaphthol analogous to scarlet S. Azococcin 7 B is a difficultly soluble brown powder. The magenta-coloured solution gives a brownish-red precipitate with hydrochloric acid, and with soda a violet-red precipitate soluble in water. Croceïn B is brown-red, difficultly soluble to a magenta-coloured solution which is precipitated violet by hydrochloric acid, and gives a violet coloration with soda. *Archil red* is homologous with scarlet S, containing two xylene- instead of two benzene-residues.

THE TETRAZO-DYES are characterised by their behaviour on reduction. With tin and hydrochloric acid, or other acid reducing agent, the decomposition is complete; but when treated with zinc and ammonia only partial decomposition ensues, and the decolorised and filtered solution usually acquires a yellow colour on exposure to air, the colourless hydrazo-compound formed being oxidised to acid yellow and amido-azobenzene or some allied body. (See below.)

A further distinction between the various red tetrazo-dyes containing a naphthol nucleus is to be found in their behaviour when treated in the solid state with strong sulphuric acid, as is shown in the following table:—

Dye.	Colour with Sulphuric Acid.		Products of Reduction.	
	With Strong Acid.	On Dilution with Water.	In Alkaline Solution.	In Acid Solution.
A —				
Biebrich scarlet.	Green.	Blue, brown, and brown precipitate.	Amido-β-naphthol and amido-hydrazobenzene-disulphonic acid (oxidising with yellow colour).	Amido-β-naphthol sulphanilic acid, and para-diamido-benzene-sulphonic acid.
Fast scarlet.	Green.	Blue; then blue-red changing to scarlet.	Amido-β-naphthol para-diamido-benzene and amido-hydrazo-benzene sulphonic acid (oxidising with yellow colour).	...
B —				
Scarlet S. Ponceau SS extra.	Violet.	Violet ppte.	Amido-β-naphthol-disulphonic acid and amido-azobenzene.	Sulphuric acid, amido-β-naphthol, aniline, and para-diamido-benzene.
Brilliant croceïn M.	Reddish-violet.	Blue-violet; and red or brown ppt. on further dilution.	...	...
Azococcin 7 B.	Bluish-violet.	Brownish-red ppte.	...	...
Croceïn B.	Violet.	Violet ppte.	...	...
C —				
Croceïn scarlet 3 B.	Indigo-blue.	Yellow-brown ppte., and then red solution.	Amido-β-naphthol-α-sulphonic acid and amido-hydrazo-benzene sulphonic acid (oxidising to acid yellow).	Sulphuric acid, amido-β-naphthol, sulphanilic acid, and para-diamido-benzene.
Croceïn scarlet 7 B.	Blue.	Violet-red.	...	...
Orseillin 2 B.	Blue.	Red.	...	...
Ponceau S extra.	Blue.	Yellowish-red.	...	...

From this table it appears that (*A*) when the sulphonic group (SO_3H) exists in the benzene nucleus or nuclei only, as in Biebrich scarlet, a green coloration is produced; (*B*) when the naphthol nucleus is alone sulphonated, as in scarlet S, the dye dissolves in strong sulphuric acid with violet colour; while (*C*) when both the benzene and naphthol or naphthalene residues are sulphonated, as in the croceïn scarlets, a blue coloration is obtained.[1]

SOUDAN III, or Amido-azobenzene-azobetanaphthol. $C_6H_5.N_2.C_6H_4.N_2.C_{10}H_6.OH.^{\beta}$ This is the only unsulphonated tetrazo-dye of commercial interest. It forms a brown powder insoluble in water, but soluble in alcohol. It dissolves in concentrated sulphuric acid with bluish-green colour, becoming blue on addition of water, and giving a red precipitate on further dilution.

TETRAZO-BROWNS mostly belong to the class of bodies sometimes called disazo-compounds, the constitution of which is supposed to be somewhat different from that of the ordinary tetrazo-compounds. The following colouring matters of this class occur in commerce:—

Resorcin brown, .	$C_6H_2(OH)_2:\left\{\begin{array}{l}N:N.C_6H_3(CH_3)_2\\N:N.C_6H_4(SO_3Na)\end{array}\right.$
Fast brown (Bayer), .	$C_6H_2(OH)_2:\left\{\begin{array}{l}N:N.C_{10}H_6(SO_3Na)^{\beta}\\N:N.C_{10}H_6(SO_3Na)^{\beta}\end{array}\right.$
Acid brown G, .	$C_6H_2(NH_2)_2:\left\{\begin{array}{l}N:N.C_6H_5\\N:N.C_6H_4(SO_3Na)\end{array}\right.$
Acid brown R, .	$C_6H_2(NH_2)_2:\left\{\begin{array}{l}N:N.C_6H_5\\N:N.C_{10}H_6(SO_3Na)\end{array}\right.$
Fast brown G (Tillmann's),	$C_{10}H_5(OH)^{\alpha}:\left\{\begin{array}{l}N:N.C_6H_4(SO_3Na)\\N:N.C_6H_4(SO_3Na)\end{array}\right.$
Fast brown (Meister),	$C_{10}H_5(OH)^{\alpha}:\left\{\begin{array}{l}N:N.C_6H_2(CH_3)_2(SO_3Na)\\N:N.C_6H_2(CH_3)_2(SO_3Na)\end{array}\right.$

RESORCIN BROWN. $C_6H_3(CH_3)_2.N_2.C_6H_2(OH)_2.N_2.C_6H_4(SO_3Na)$. This compound is one of the few tetrazo-colours not containing a naphthalene nucleus. It is a brown powder, soluble in water to a brown solution which is but slightly changed by soda, but yields a brown precipitate with hydrochloric acid. The solid dye dissolves in strong sulphuric acid with brown colour, and on dilution with water a brown precipitate is formed.

ACID BROWN G is the type of several similar bodies obtained by introducing an amine residue instead of a phenol residue. It is prepared by the action of diazobenzene chloride on chrysoïdine-sulphonic acid. It dissolves in strong sulphuric acid with reddish-brown colour, becoming yellowish on dilution with water.

---

[1] **AZORUBIN 2 S**, produced by reacting on diazotised acid yellow with Nevile's α-naphthol-sulphonic acid from napthionic acid (and hence a dye of class C) appears to be an exception to this rule, for it dissolves in sulphuric acid with green colour, becoming blue on dilution.

Acid Brown R is a similar dye prepared by the action of diazotised napthionic acid on chrysoïdine. It is a brown powder, forming a brown aqueous solution which is unchanged by alkalies, but precipitated brown by acids. In strong sulphuric acid the dye dissolves with a dirty olive colour, and on dilution gives first a reddish and then a brown precipitate.

Fast Brown G is a brown powder, forming a reddish-brown solution. Dilute hydrochloric acid gives a violet precipitate, soluble in excess with violet colour, or in water with brown colour. Alkalies turn the aqueous solution cherry-red. Strong sulphuric acid dissolves the solid dye with violet colour, becoming yellowish-brown on dilution.

Fast Brown of Meister, Lucius, and Brüning is homologous with the last dye, and forms a dark brown powder soluble in water with brown colour. Alkalies turn the solution reddish-yellow, and dilute acids give a violet precipitate. Strong sulphuric acid dissolves the dye with violet colour, becoming red on dilution. The colour produced on wool is a brownish-red.

Naphthol Black or **Azo-Black** contains $C_{10}H_5(SO_3Na)_2.N_2.C_{10}H_6.N_2.C_{10}H_4(OH)^{\beta}(SO_3Na)_2$, and results from the action of salt R on diazotised amido-azonaphthalene-disulphonic acid. It forms a readily soluble black powder, yielding a dark blue-violet aqueous solution, precipitated red-violet by hydrochloric acid, and giving with alkalies a blue precipitate soluble in much water. Precipitates are yielded with barium and calcium chlorides, as also by solutions of iron and other heavy metals. The dye dissolves in strong sulphuric acid with dark green colour, becoming blue on dilution. Naphthol black dyes silk and wool a blue-black in a slightly acid bath.

Wool-Black is a similar dye produced by the reaction of diazotised amido-azobenzene-disulphonic acid on paratolyl-beta-naphthylamine, and has the formula, $C_6H_4(SO_3Na).N_2.C_6H_3(SO_3Na).N_2.C_{10}H_6.NH(C_7H_7)$. It gives a violet precipitate with soda, and a red-violet precipitate with hydrochloric acid; and dissolves in strong sulphuric acid with blue colour, yielding a brown precipitate on dilution.[1]

---

[1] Both wool-black and azo-black are employed as indigo-substitutes in wool-dyeing. They are fairly fast, and can be applied in the simplest possible manner, namely, by simply immersing the wool in an acid bath of the dye, but the colour is apt to bleed in the milling process.

Azo-Dyes from Benzidine and its Analogues.[1]

During the last few years a group of new coal-tar dyes have been introduced, which possess the characteristic property of dyeing cotton in a neutral or alkaline bath without a mordant, a peculiarity previously confined to a few natural colouring matters (*e.g.*, turmeric, safflower, annatto). The new dyes belong to the class of tetrazo- or secondary azo-compounds, but differ from those previously described (page 196 *et seq.*) by containing two benzene nuclei in the azo-group, being derived from diazo-diphenyl (diazotised benzidine) or its analogues. They all contain a sulpho- or carboxyl group, and occur in commerce as sodium salts.

When an alcoholic solution of nitrobenzene is treated with caustic soda and zinc-dust, azobenzene, $C_6H_5.N_2.C_6H_5$, is formed. This body is converted by boiling with zinc-dust into hydrazo-benzene, $C_6H_5.NH.NH.C_6H_5$, and this on treatment with strong hydrochloric acid is converted by a molecular change into benzidine, which is precipitated on adding excess of ammonia.

Benzidine has the constitution of a diamido-diphenyl in which both the NH_2 groups occupy the para-position. When the dihydrochloride is treated in acid solution with nitrous acid or sodium nitrite it is diazotised, forming tetrazo-diphenyl dichloride, according to the following equation:—

$$\left\{\begin{array}{l} C_6H_4.NH_2^p.HCl \\ C_6H_4.NH_2^p.HCl \end{array}\right. + 2HNO_2 = 4H_2O + \left\{\begin{array}{l} C_6H_4.N{:}N.Cl \\ C_6H_4.N{:}N.Cl \end{array}\right.$$

By reaction with aromatic amines or phenols, or their derivatives, the tetrazo-diphenyl dichloride forms the series of colouring matters known as the benzidine dyes, of which *congo-red* is the type. To produce this substance, the solution of one molecule of tetrazo-diphenyl dichloride is added to a well-cooled solution of two molecules of sodium naphthionate, and then sodium acetate added:—

$$\left\{\begin{array}{l} C_6H_4.N_2.Cl \\ C_6H_4.N_2.Cl \end{array}\right. + 2C_{10}H_6(SO_3Na)NH_2$$

$$= 2HCl + \left\{\begin{array}{l} C_6H_4.N_2.C_{10}H_5(SO_3Na).NH_2 \\ C_6H_4.N_2.C_{10}H_5(SO_3Na).NH_2. \end{array}\right.$$

The reaction requires several hours for its completion, and occurs in two distinct stages, an intermediate product being first obtained. This is of general occurrence under similar circumstances, and by taking advantage of the fact it is possible to combine one molecule of diazotised benzidine or an analogous body with two different phenols, amines, &c. Thus *congo corinth* is obtained by first reacting on one molecule of tetrazo-diphenyl dichloride with one molecule of sodium alphanaphthylamine - sulphonate, and treating the intermediate product thus obtained with sodium alphanaphthol-sulphonate:—

---

[1] A very valuable paper on the Benzidine and Allied Colours, from which much of the information in the text is derived, has been published by G. H. Hurst (*Jour. Soc. Dyers, &c.*, iv. 14).

$$\left\{\begin{array}{l}C_6H_4.N_2.C_{10}H_5(SO_3Na)^a.NH_2^a\\ C_6H_4.N_2.Cl\end{array}\right. + C_{10}H_6(SO_3Na)^a.OH^a$$

$$= HCl + \left\{\begin{array}{l}C_6H_4.N_2.C_{10}H_5(SO_3Na)^a.NH_2^a\\ C_6H_4.N_2.C_{10}H_5(SO_3Na)^a.OH^a.\end{array}\right.$$

By processes similar to those employed for the preparation of benzidine, the homologous base tolidine, $(NH_2).C_6H_3(CH_3).C_6H_3(CH_3).(NH_2)$, can be prepared from nitrotoluene, $C_6H_4(CH_3)(NO_2)$; and when diazotised, tolidine yields tetrazo-ditolyl dichloride, homologous with the similar product from benzidine. This body reacts with phenols, aromatic amines, &c., in the same way as its lower homologue. *Benzopurpurin* and *azo-blue* are examples of colouring matters thus obtained.

By first sulphonating paranitrotoluene, and treating the product with zinc-dust and caustic soda, it is converted into diamido-stilbene-disulphonic acid, and this when diazotised in hydrochloric acid solution yields the dichloride of tetrazo-stilbene-disulphonic acid:—

$$\left\{\left\{\begin{array}{l}CH.C_6H_3(SO_3H).NH_2\\ CH.C_6H_3(SO_3H).NH_2\end{array}\right.\right. + 2HNO_2$$

$$= 4H_2O + \left\{\left\{\begin{array}{l}CH.C_6H_3(SO_3H).N_2.Cl\\ CH.C_6H_3(SO_3H).N_2.Cl.\end{array}\right.\right.$$

This body can react with phenols, amines, &c., to form colouring matters, of which *brilliant yellow* and the *Hessian purples* are examples.

Similar colouring matters are obtainable from diamido-fluorene, $C_{13}H_8(NH_2)_2$.

As already stated, all the colouring matters of the class under consideration dye cotton in a neutral or slightly alkaline bath, without the aid of a mordant. In practice, the cotton is boiled in a solution of the dye rendered alkaline by soap and sodium phosphate or carbonate. Borate, silicate, and stannate of sodium are also used.

The benzidine dyes can also be used for wool, but an alkaline bath is an objection. With some of them a bath acidulated with acetic acid can be employed. The colours produced on wool by the blue and violet dyes of this class are always much redder in shade than are given by the same dyes on cotton. The colours on wool are faster to light than those on cotton.

Commercial Name.	Obtained by the Reaction in Alkaline Solution of	Formula or Chemical Nature.	Colour produced on Cotton.
From Benzidine.			
Chrysamine G. Flavophenine.	1 Diazotised benzidine. 2 Salicylic acid.	$C_6H_4.N_2{}^1.C_6H_3(ONa)^p.COOH^m$ $C_6H_4.N_2{}^1.C_6H_3(ONa)^p.COOH^m$	Canary yellow.
Congo Yellow.	1 Diazotised benzidine. 1 Phenol. 1 Sulphanilic acid.	$C_6H_4.N_2{}^1.C_6H_4.(OH)^p$ $C_6H_4.N_2{}^1.C_6H_3(SO_3Na)^1.(NH_2)^p$	Yellow, with slight orange shade.
Congo Red.	1 Diazotised benzidine. 2 Naphthionic acid.	$C_6H_4.N_2{}^{\beta}C_{10}H_5(SO_3Na)^{\alpha}.NH_2$ $C_6H_4.N_2{}^{\beta}C_{10}H_5(SO_3Na)^{\alpha}.NH_2{}^{\alpha}$	Scarlet.
Deltapurpurin G.	1 Diazotised benzidine 2 β-naphthylamine sulphonic acid.	$C_6H_4.N_2{}^{\alpha}_{\alpha}C_{10}H_5(SO_3Na).NH_2{}^{\beta}$ $C_6H_4.N_2\ C_{10}H_5(SO_3Na).NH_2{}^{\beta}$	Yellow shade of scarlet.
Brilliant Congo G.	1 Diazotised benzidine. 1 β-naphthylamine-disulphonic acid. 1 β-naphthylamine-monosulphonic acid.	$C_6H_4.N_2.C_{10}H_4(SO_3Na)_2.NH_2{}^{\beta}$ $C_6H_4.N_2.C_{10}H_5(SO_3Na).NH_2{}^{\beta}$	Scarlet.
Heliotrope.	1 Diazotised diamido-diphenetoil. 2 Methyl-naphthylamine sulphonic acid.	$C_6H_3(OC_2H_5).N_2.C_{10}H_5(SO_3Na).NH(CH_3)$ $C_6H_3(OC_2H_5).N_2.C_{10}H_5(SO_3Na).NH(CH_3)$	Crimson shade of red.
Congo Corinth.	1 Diazotised benzidine. 1 α-naphthylamine sulphonic acid. 1 α-naphthol sulphonic acid.	$C_6H_4.N_2.C_{10}H_5(SO_3Na)^{\alpha}.NH_2{}^{\alpha}$ $C_6H_4.N_2.C_{10}H_5(SO_3Na)^{\alpha}.OH^{\alpha}$	Deep purplish-red.
Azo-Violet.	1 Diazotised diamido-diphenetoil. 1 Naphthylamine sulphonic acid. 1 Naphthol sulphonic acid.	$C_6H_3(OC_2H_5).N_2.C_{10}H_5(SO_3Na).NH_2$ $C_6H_3(OC_2H_5).N_2.C_{10}H_5(SO_3Na).OH$	Dark blue violet.
Benzoazurin R.	1 Diazotised anisidine diamido-dianisoil. 2 α-naphthol sulphonic acid	$C_6H_3(OCH_3).N_2.C_{10}H_5(SO_3Na)^{\alpha}.OH^{\alpha}$ $C_6H_3(OCH_3).N_2.C_{10}H_5(SO_3Na)^{\alpha}.OH^{\alpha}$	Dark blue.
Benzoazurin G.	...	Homologue of benzo-azurin R, containing C_2H_5 groups in place of CH_3.	Blue.
From Tolidine.			
Chrysamine R.	...	Homologue of chrysamine G.	Bright yellow.
Benzopurpurin 4 B.	...	Homologue of congo-red.	Crimson-red.
Benzopurpurin 6 B.	...	Isomer of benzopurpurin 4 B.	Crimson-red.

Commercial Name.	Obtained by the Reaction in Alkaline Solution of	Formula or Chemical Nature.	Colour produced on Cotton.
Benzopurpurin B.	1 Diazotised tolidine. 2 β-naphthylamine-δ-sulphonic acid.	Isomer of benzopurpurin 4 B.	Bright red.
Deltapurpurin 5 B.	...	Homologue of deltapurpurin G.	Scarlet.
Diamine red 3 B.	...	Isomer of deltapurpurin 5 B.	Scarlet.
Congo 4 R.	1 Diazotised tolidine. 1 Naphthionic acid. 1 Resorcinol.	$\begin{cases} C_6H_3(CH_3).N_2.C_{10}H_5(SO_3Na)^{\alpha}.NH_2^{\alpha} \\ C_6H_3(CH_3).N_2.C_6H_4(OH)_2 \end{cases}$	Crimson.
Rosazurin G.	1 Diazotised tolidine. 1 β-naphthylamine-δ-sulphonic acid. 1 Ethyl-β-naphthylamine δ-sulphonic acid.	$\begin{cases} C_6H_3(CH_3).N_2.C_{10}H_5(SO_3Na)^{\delta}.NH_2^{\beta} \\ C_6H_3(CH_3).N_2.C_{10}H_5(SO_3Na)^{\delta}.NH(C_2H_5)^{\beta} \end{cases}$	Scarlet.
Rosazurin B.	...	Ethyl-derivative of rosazurin G.	Bluish-crimson.
Brilliant Congo R.	...	Homologue of brilliant congo G.	Scarlet.
Congo Corinth B.	...	Homologue of congo corinth.	Dark reddish-violet.
Azo-blue.	1 Diazotised tolidine. 2 α-naphthol sulphonic acid.	$\begin{cases} C_6H_4.N_2.C_{10}H_5(SO_3Na)^{\alpha}OH^{\alpha} \\ C_6H_4.N_2.C_{10}H_5(SO_3Na)^{\alpha}OH^{\alpha} \end{cases}$	Violet-blue.
FROM DIAMIDO-STILBENE.			
Brilliant Yellow.	1 Tetrazo-stilbene disulphonic acid. 2 Phenol	$\left\{\begin{cases} CH.C_6H_3(SO_3Na).N_2.{}^1C_6H_4(OH)^p \\ CH.C_6H_3(SO_3Na).N_2.{}^1C_6H_4(OH)^p \end{cases}\right.$	Orange yellow.
Chrysophenine.	...	The hydrogen of the OH groups of brilliant yellow replaced by methyl or ethyl.	Sulphur yellow.
Hessian Yellow.	1 Tetrazo-stilbene disulphonic acid. 2 Salicylic acid.	$\left\{\begin{cases} CH.C_6H_3(SO_3Na).N_2{}^1.C_6H_3(OH)^p.COONa \\ CH.C_6H_3(SO_3Na).N_2{}^1.C_6H_3(OH)^p.COONa \end{cases}\right.$	Bright orange-yellow.
Hessian Red.	1 Tetrazo-stilbene disulphonic acid. 2 Naphthionic acid.	$\left\{\begin{cases} CH.C_6H_3(SO_3Na).N_2.C_{10}H_5(SO_3Na)^{\alpha}.NH_2^{\alpha} \\ CH.C_6H_3(SO_3Na).N_2.C_{10}H_5(SO_3Na)^{\alpha}.NH_2^{\alpha} \end{cases}\right.$	Red.
Hessian Purples B, P, D.	...	Isomers of Hessian red.	Purple red.
Hessian Purple N.	1 Tetrazo-stilbene disulphonic acid. 2 β-naphthylamine.	$\left\{\begin{cases} CH.C_6H_3(SO_3Na).N_2.C_{10}H_6.NH_2^{\beta} \\ CH.C_6H_3(SO_3Na).N_2.C_{10}H_6.NH_2^{\beta} \end{cases}\right.$	Deep red.
Hessian Violet.	1 Tetrazo-stilbene disulphonic acid. 1 α-naphthylamine. 1 β-naphthol.	$\left\{\begin{cases} CH.C_6H_3(SO_3Na).N_2.C_{10}H_6.NH_2^{\alpha} \\ CH.C_6H_3(SO_3Na).N_2.C_{10}H_6.OH^{\beta} \end{cases}\right.$	Dark bluish-violet.

Colouring Matter.	Appearance and Solubility.	Reaction of Aqueous Solution with			Colour with strong Sulphuric Acid.
		Caustic Soda.	Dilute Acids.	Magenta.	
Chrysamine G and B.	See page 206.	Orange-red.	Orange flakes.	...	Crimson.
Congo Yellow.	Brownish-yellow paste; difficultly soluble.	Red.	Brown-yellow precipitate.	...	Brown-red.
Brilliant Yellow.	See page 208.	Scarlet colour.	Blue-black precipitate.	Precipitated.	Crimson.
Chrysophenine.	See page 208.	No change.	Dark brown-red precipitate.	...	Red-violet.
Hessian Yellow.	Yellow-brown powder; readily forming yellowish-orange solution.	Scarlet colour.	Green-brown precipitate.	...	Bright crimson.
Congo Red.	See page 206.	No change.	Blue colour or precipitate.	...	Slate-blue.
Brilliant Congo G.	Brick-red crystal powder; difficultly soluble to orange-scarlet solution.	No change.	Violet precipitate.	Precipitated.	Blue.
Brilliant Congo R.	Brownish-red crystalline powder; solution orange-scarlet.	No change.	Brown precipitate.	Precipitated.	Blue.
Congo 4 R.	Dark red powder; not very soluble.	No change.	Purple-red precipitate.	...	Blue.
Benzopurpurin B.	See page 207.	No change.	Brown-red precipitate.	...	Blue.
Benzopurpurin 4 B.	See page 207.	No change.	Red-brown precipitate.	...	Blue.
Benzopurpurin 6 B.	Red powder; not very soluble.	No change.	Blue precipitate.	...	Blue.
Deltapurpurin G.	Brick-red powder; not very soluble; turbid orange-scarlet solution.	No change.	Dark red-brown precipitate.	Precipitated.	Blue.
Deltapurpurin 5 B.	Dark brown-red powder; sparingly soluble to orange-red solution.	No change.	Brown precipitate.	Precipitated.	Blue.
Diamine Red 3 B.	Dark brown-red powder; scarlet solution.	Scarlet precipitate in reddish solution.	Red-brown precipitate in yellow-brown solution.	Precipitated.	Dark blue.
Rosazurin G.	Dark red powder; sparingly soluble to reddish-orange solution.	Red-orange.	Brownish-violet precipitate.	...	Deep blue.
Rosazurin B.	Brown-red powder; sparingly soluble.	Red-orange.	Crimson precipitate.	...	Red-violet.
Congo Corinth.	Dark greenish powder; dissolving readily to deep crimson solution.	Crimson coloration.	Violet-blue precipitate.	Precipitated.	Deep blue.
Congo Corinth B.	Brownish-black powder; not readily soluble.	Bright crimson precipitate.	Violet-blue precipitate.	Precipitated.	Deep blue.
Heliotrope.	Purple-brown powder; readily soluble.	Red colour.	Violet precipitate.	...	Blue.
Azo-Violet.	Brown-black powder; not very soluble to reddish-violet solution.	Bright crimson colour.	Dark blue precipitate.	Precipitated.	Blue.
Hessian Purple N.	Brown-red powder; imperfectly soluble to scarlet solution.	Scarlet precipitate.	Indigo-blue precipitate.	Precipitated.	Greenish-blue.
Hessian Purple B.	Brown-red powder; completely soluble.	Crimson precipitate.	Dark blue precipitate.	...	Violet.
Hessian Violet.	Black powder; readily soluble.	Red precipitate.	Blue precipitate.	...	Blue.
Violet Black.	Bronze powder; dark violet or brown-red solution.	Blue-violet solution.	Red-violet precipitate.	Precipitated.	Blue.
Benzo-azurin R.	See page 208.	Crimson colour.	Violet precipitate.	...	Blue.
Benzo-azurin G.	Blue-black powder; readily soluble to blue-violet liquid.	Bright crimson colour.	Darkening and violet precipitate.	Precipitated.	Blue.
Azo-Blue.	See page 208.	Crimson colour.	Dark blue colour or precipitate.	...	Blue.

The preceding tables show the constitution and reactions of the more important dyes from benzidine and its analogues. The table on last page has been mainly compiled from the recorded observations of E. Knecht and G. H. Hurst (*Jour. Soc. Dyers, &c.*, v. 14).

The colouring matters named in the foregoing tables may be distinguished from all other azo-dyes by heating a piece of unmordanted cotton in the aqueous solution. The cotton is then removed to a warm solution of soap, which will strip the dye from the fibre unless the colour be derived from benzidine or an analogous diamine.

The dyes from benzidine, &c., can be fixed on silk from a bath containing soap and phosphate of sodium; and mixed silk and cotton goods take the colour well and evenly.

The benzidine dyes act as mordants to the basic aniline dyes, a fact of which the practical application is evident.

In their general reactions with sulphuric acid and reducing agents the benzidine and analogous colours resemble the other azo-dyes (page 210).

Besides the dyes mentioned in the foregoing tables, there are a few other colouring matters of peculiar constitution, such as *azarine* and *primulin*, which can be conveniently considered in the same section, and are described in detail on page 209 *et seq.*

The following is a detailed description of the more important of the dyes from benzidine and its analogues:—

CHRYSAMINE, or FLAVOPHENINE, is produced by the action of tetrazo-diphenyl chloride on sodium salicylate. It forms a yellow powder, sparingly soluble in cold but readily in boiling water. The solution has an orange colour, changed by caustic soda to an orange-red, from which acids precipitate tetrazodiphenyl-disalicylic acid in orange flakes soluble in ether. Strong sulphuric acid dissolves the solid dye with deep magenta colour.

CONGO-RED forms a brownish-red powder, readily soluble in water to produce a blood-red solution. Very small quantities of dilute acids turn the liquid to a beautiful blue, a precipitate of the free sulphonic acid being formed in strong solutions. Alkalies restore the red colour, and salts of neutral constitution, such as alum,[1] ferrous sulphate, cupric sulphate, &c., do not act as acids. Hence it has been proposed to employ congo-red as an indicator of neutrality, but it has been shown by R. T. Thompson (*Jour. Soc. Chem. Ind.*, vi. 195) that its delicacy has been overrated.[1] While not wholly unaffected by weak acids, such as carbonic and sulphydric, it fails to indicate the presence of acetic acid in presence of twelve times the quantity of sodium acetate. Congo-red dissolves in strong sulphuric acid with slate-blue colour, which is not changed by dilution. Congo-red dyes cotton a bright crimson-red, but the colour is far from permanent. Exposure to light and air for a short period dulls the colour, which is restored to its original brightness on soaping. After longer exposure to light, the colour cannot be thus restored. On wool the colour is rather more scarlet, brighter, and more stable than on cotton.

---

[1] R. T. Thompson finds that congo-red is incapable of indicating with certainty the presence of 0·2 per cent. of sulphuric acid in alum, or even of giving a trustworthy reaction with 0·5 per cent.

Benzopurpurin 4 B is the next higher homologue of congo-red. It forms a dark brownish-red powder, soluble in water with orange-red colour, which is unchanged by alkalies. From strong solutions, dilute acids throw down the free sulphonic acid as a reddish-brown precipitate resembling ferric hydroxide. Strong sulphuric acid dissolves the solid dye with pure blue colour, a blue precipitate being formed on dilution. In a hot bath containing soap or alkaline carbonate, benzopurpurin dyes cotton a fine scarlet. The colour is almost unaffected by dilute acids, and is much faster to light than congo-red.

Benzopurpurin B is isomeric with the last named dye, and is prepared by the reaction of diazotised tolidine on β-naphthylamine-sulphonic acid[2] in presence of alkali. It is a brownish-red powder, not very soluble in water. The aqueous solution is reddish-brown, unchanged by alkalies, and precipitated brownish-red by dilute acids. It dyes cotton a colour approaching turkey-red in tint of brilliancy. Acids turn the dyed fibre blue, the colour being restored by alkalies or washing.

Deltapurpurin G is isomeric with congo-red, and like its homologue *Deltapurpurin 5 B* is obtained by the use of the so-called δ-modification of β-naphthylamine-sulphonic acid.[3] The delta-purpurins dye cotton a bright scarlet. Deltapurpurin 5 B is distinguished from its isomer *diamine red 3 B*[1] and from *D delta-purpurine 7 B* by not being precipitated from its aqueous solution by acetic acid, and by forming a soluble calcium salt.

---

[1] Chrysamine is probably the only commercial azo-dye which is extracted by agitating its acidulated aqueous solution with ether.

[2] The sulphonic acid is the so called β-modification, obtained (mixed with the α- and γ-isomerides) by heating β-naphthylamine with 8 parts of sulphuric acid (96–97 per cent. of H_2SO_4) to 100°–105° C. for six hours, or by heating Schäffer's β-naphthol-sulphonic acid with ammonia.

[3] The β-naphthylamine-δ-sulphonic acid, used for the production of the *deltapurpurins*, is prepared by heating β-naphthylamine sulphate with 5 or 6 parts of strong sulphuric acid (1·845 specific gravity) to 150° C. for 1½ hour. The α- and γ- sulphonic acids of β-naphthylamine are said to be transformed into the β-modification by this treatment.

Azo-Blue is closely related in constitution to benzopurpurin, the two NH_2 groups of the latter being replaced by two of OH. It forms a bluish-black powder, readily soluble in water with fine violet colour, which is changed to crimson by caustic alkalies and restored by dilute acids. In the concentrated solution, hydrochloric acid produces a violet-blue precipitate, but dilute acetic acid occasions no change. Concentrated sulphuric acid dissolves the dye with pure blue colour, the solution giving a violet precipitate on dilution with water. In a boiling hot bath containing soap and sodium phosphate, azo-blue dyes cotton a violet-blue colour, fast to soap, and unaffected by acids.

Benzo-azurin R forms a dark blue (almost black) powder, with a slight bronze reflex. It dissolves readily in water with deep violet-blue colour, changed by caustic potash to a red-violet or crimson. Dilute hydrochloric acid produces a dark violet precipitate. The dye dissolves in strong sulphuric acid with pure blue colour. Benzo-azurin dyes cotton a dark shade of blue. The colour is remarkably fast to light, and unaffected by acids, but is reddened by alkalies.

Benzo-azurin G differs from the last named dye in not being precipitated from its solution by dilute acids, the colour being simply darkened. On cotton it dyes a brighter colour than the last, and on wool gives a pleasant and useful shade of violet.

Brilliant Yellow forms a readily soluble brown powder. The solution is orange, changed to scarlet by alkalies, and gives a blue-black precipitate with dilute acids. It dyes cotton and wool a very bright orange shade of yellow, quite fast to light. Acids change the colour fibre to blue, and alkalies redden it; soaping turns it a shade redder, but there is no bleeding.

On treating brilliant yellow with soda it forms a red basic salt, and on ethylating this body it is converted into

Chrysophenine. This forms a light orange powder, partially soluble in water. The solution is unchanged by alkalies, but gives a dark brownish-red precipitate with acids. In a neutral bath it dyes both wool and cotton a bright yellow, unaffected by dilute acids, alkalies, or soap.

---

[1] Prepared by acting on diazotised tolidine in alkaline solution with β-naphthylamine-F-sulphonic acid. This is prepared by fusing the sodium salt of α-naphthalene-disulphonic acid with four times its weight of 50 per cent. caustic soda at 200° C., until dioxynaphthalene begins to be formed. β-naphthol-F-sulphonic acid is formed, and on heating this with ammonia under pressure the corresponding amido-acid is obtained.

Azarine is a colouring matter of peculiar constitution, being represented by the following formula:—

$$SO_2\left\{\begin{array}{l}C_6H_3(OH).NH.N(SO_3NH_4).C_{10}H_6.OH\\ C_6H_3(OH).NH.N(SO_3NH_4).C_{10}H_6.OH\end{array}\right.$$

It is produced by diazotising diamido-dihydroxybenzosulphone, $SO_2(C_6H_3(OH).NH_2)_2$, and causing the product to react with betanaphthol. The azo-compound formed is then treated with acid sulphite of ammonium or sodium, which forms a compound of the nature shown above. The employment of azarine is an application of the fact that many azo-compounds which are themselves insoluble combine with the acid sulphites of the alkali-metals to form compounds which are soluble in water and unaffected by dilute acids, but which under the influence of heat are decomposed into a bisulphite of alkali-metal and an insoluble azo-dye. The reaction is capable of being used in calico-printing.

Azarine occurs in commerce in the form of an orange-yellow paste, closely resembling alizarin paste. It is sparingly soluble in water, but dissolves readily in alkalies with bluish-violet colour. The aqueous solution is yellow, and yields an orange-yellow precipitate with hydrochloric acid, and with caustic soda a violet precipitate, which dissolves to a red solution on heating. On heating the paste, sulphur dioxide is evolved, and the colour changes to scarlet. Strong sulphuric acid dissolves azarine paste with magenta-red colour, a reddish-brown precipitate being formed on dilution. Azarine forms alumina-lakes of a fine red colour with a shade of violet. It is very fast to soap and chlorine, but is affected by light.

Primulin is a colouring matter the constitution of which has not yet been made public, except to the extent that it is an amido-sulphonic acid (A. G. Green, *Jour. Soc. Dyers, &c.*, iv. 39). The commercial product is a yellow powder, which is very soluble in hot water. The very dilute aqueous solution of primulin exhibits a blue fluorescence. In a 5 per cent. neutral bath at a boiling temperature, primulin dyes cotton a lemon-yellow colour, which is tolerably fast to scouring, entirely unaffected by alkalies, and turned a golden yellow by acids. The affinity of the fibre for the colouring matter is increased, and consequently deeper shades may be obtained, by addition of sodium chloride or sulphate to the bath. Reducing agents produce no change, but the colour is attacked by oxidising agents, such as bleaching powder or chromic acid. By the latter the shade is changed to olive, while boiling solutions of hypochlorites turn the colour to orange-yellow, which is very fast to all agents.

Since primulin contains an amido-group, it is capable of being diazotised, and this operation may be readily performed on the dyed fibre by passing the washed material through a dilute solution of sodium nitrite (3 to 5 per cent.) acidulated with sulphuric acid. If the fabric be then again washed and immersed without delay in a developing solution of one of the naphthols, naphthylamines, or their derivatives, various shades of yellow, orange, scarlet, or maroon may be obtained. The colours so obtained are termed *ingrain colours*, and are characterised by their extraordinary fastness to scouring, milling, acids, &c., being said to be only equalled in this respect by alizarin and its congeners, and to far exceed the ordinary benzidine dyes.

General Analytical Reactions of Azo-Dyes.

The great majority of the azo-dyes are sulphonated, and more or less soluble in water. In no case is a sulphonated dye removed from its aqueous solution by agitation with ether, whether the liquid be alkaline or acid. There are a limited number of unsulphonated azo-dyes, such as *chrysoïdine* and *bismarck brown*, from which the free base may be extracted by agitating the alkaline solution with ether. *Chrysamine*, on the other hand, is an unsulphonated azo-dye of acid character, and is removed from its acidulated aqueous solution on agitation with ether.

The azo-dyes are stated to be non-poisonous. On addition of hydrochloric acid to the concentrated aqueous solution of a hydroxyazo-dye, a precipitate is usually produced if the colouring matter contain only one SO_3H group, as in that case the free sulphonic acid often is insoluble or sparingly soluble in water. But when the free acid contains two sulphonic groups it is soluble in water, and hence is not precipitated when the solution of the dye is acidulated.[1] Tropæolin 3 O gives a purple precipitate soluble in excess of hydrochloric acid, and some of the scarlets behave similarly.

The caustic alkalies and ammonia do not usually produce a precipitate in solutions of the sulphonated azo-dyes; but they often change the colour, owing to the replacement of the hydrogen of the hydroxyl groups.[2]

---

[1] This statement does not apply to the benzidine dyes, almost all of which are precipitated by dilute acid.

[2] Thus a mere trace of alkali changes the dilute solution of mandarin from yellow to crimson (exactly the opposite being true of methyl-orange). Scarlets G and R and croceïn and biebrich scarlets show a similar reaction but are far less sensitive than mandarin. Ammonia is almost without action on solutions of scarlets 2 R and 3 R.

The concentrated solutions of many of the azo-dyes are precipitated by barium and calcium chlorides, and in some cases the reactions are of analytical interest. The azo-dyes as a class are remarkable for the striking colorations produced when the solid substance is treated with concentrated sulphuric acid, as was first pointed out by J. Spiller (*Chem. News*, xlii. 191). To apply the test it is merely necessary to heat a few grains of the solid substance in a test-tube or porcelain crucible with strong sulphuric acid. Very frequently, useful information can be gained by observing the spectrum of the coloured liquid obtained. In the case of the tetrazo-dyes the colour of the solution in strong sulphuric acid is an important indication of the constitution of the colouring matter (see page 198).

Among the most characteristic reactions of the azo-dyes is their behaviour with reducing agents, the most generally suitable reagent for the purpose being hydrochloric acid and zinc or solution of stannous chloride. Thus the amido-azo-compounds are split up into a primary amine and para-diamine, amido-azobenzene yielding aniline and paraphenylene-diamine (para-diamido-benzene):—$C_6H_5.N{:}N.C_6H_4.NH_2 + 2H_2 = C_6H_5.NH_2 + C_6H_4(NH_2)_2$.

Similarly, when helianthin is reduced it yields the ammonium salt of sulphanilic acid (amidobenzene-sulphonic acid) and dimethyl-paradiamidobenzene:—

$$\begin{aligned}&C_6H_4(SO_3NH_4).N{:}N.C_6H_4.N(CH_3)\\&= C_6H_4(SO_3NH_4)NH_2 + H_2N.C_6H_4.N(CH_3)_2.\end{aligned}$$

The best way of affecting this reduction is to heat the helianthin on the water-bath with ammonium sulphide until the orange colour disappears. The ammoniacal liquid is agitated with ether, and the ethereal layer separated from the aqueous liquid containing ammonium sulphanilate. The ethereal solution agitated with moist hydrated oxide of lead (to get rid of sulphide), filtered, and evaporated, leaves free dimethyl-paradiamido-benzene. This base melts at 41° and boils at 257°. It forms asbestos-like needles, which when pure are unchanged on exposure to air, but otherwise turn red or violet. It is readily soluble in water, alcohol, chloroform, and benzene, but less so in ether or petroleum ether. It may be purified by conversion into the sulphate and crystallising the salt from absolute alcohol. On treating the free base or a salt with a hydrochloric acid solution of sulphuretted hydrogen, a splendid blue coloration is produced, *methylene blue* being formed.

An acid solution of stannous chloride reduces the hydroxyazo-dyes in a similar manner, the products being a primary amine and an amidophenol. Thus oxyazobenzene yields aniline, $C_6H_5NH_2$, and para-amidophenol, $C_6H_4(NH_2).OH$. Mandarin splits up similarly into sulphanilic acid, $C_6H_5(SO_3H)NH_2$, and amidobetanaphthol, $C_{10}H_5(NH_2)OH$. When the naphthol group is sulphonated, the amidonaphthol-sulphonic acid decomposes into amido-naphthol and free sulphuric acid. Thus xylidine-red is decomposed as follows:—$C_6H_3(CH_3).N{:}N{:}C_{10}H_4(SO_3Na)_2.OH = + 2H_2OC_6H_3(CH_3)_2NH_2 + C_{10}H_6(NH_2).OH + 2NaHSO_4$. With an alkaline reducing agent, such as ammonium sulphide or zinc and ammonia, the amidonaphthol-disulphonic acid does not undergo decomposition.

Secondary azo-dyes split up in a similar manner under the action of reducing agents. Thus with metallic tin or stannous chloride and hydrochloric acid, biebrich scarlet yields sulphanilic acid, paradiamido-benezene, and amidonaphthol. With an alkaline reducing agent, such as zinc and ammonia, biebrich scarlet undergoes a modified decomposition, resulting in the formation of amidohydrazo-benzene sulphonate and amido-naphthol, thus:—

$$C_6H_4(SO_3Na).N{:}N.C_6H_4.N{:}N.C_{10}H_6.OH + 3H_2$$
$$= C_6H_4(SO_3Na).NH{:}NH.C_6H_4.NH_2 + C_{10}H_6(NH_2).OH\,.$$

On exposing the decolorised liquid to the air it rapidly acquires a yellow colour, from the production of sodium amido-azobenzene-sulphonate or *acid yellow*. Other tetrazo-dyes behave similarly.

Congo-red, the type of the benzidine dyes, on reduction yields benzidine and a diamidonaphthalene-sulphonic acid, $C_{10}H_5(SO_3H)_\alpha (NH_2)^\alpha(NH_2)^\beta$.

It will be seen that the investigation of the behaviour of the azo-dyes with reducing agents affords a most valuable means of recognising them and ascertaining their constitution. The bases resulting from the treatment can be extracted from the alkaline liquid with ether,[1] and if more than one be produced they can be separated by fractional distillation or crystallisation of their salts. The isolation and identification of the amidophenols is very difficult, especially as some of them are very readily affected by air. Hence it is preferable, when it is desired to obtain them in a pure state, to evaporate the neutralised solution to dryness, and heat the residue with anhydrous sodium carbonate.

The following table gives some of the leading characters of certain of the bases produced by the reduction of commercial azo-dyes:—

---

[1] Whenever an amidonaphthol-sulphonic acid is a product of the reduction, it decomposes into an amidonaphthol and free sulphuric acid, if an acid reducing agent be employed; but is not decomposed, and hence does not pass into the ether, when ammonium sulphide is used as the reducing agent.

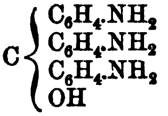
Name.	Formula.	Melting Point °C.	Boiling Point °C.	Other Characters.
Aniline. Amidobenzene. Phenylamine.	$C_6H_5.NH_2$	-8	183·7	Sparingly soluble. Violet colour with bleaching solution.
Ortho-toluidine. Ortho-amidotoluene.	$C_6H_4(CH_1)^1.NH_2^{a}$	Below - 20	198	Brown colour with bleaching solution. Colour soluble in ether, and changed to pink by dilute acetic acid.
Paratoluidine. Paramidotoluene.	$C_6H_4(CH_2)^1.NH_2$	45	198	White, crystalline. No reaction with bleaching powder. Dissolved in strong H_2SO_4, and nitric acid added, gives blue, changing to red.
Alpha-naphthyl-amine. Alpha-amidonaphthalene.	$C_{10}H_7.NH_2^{a}$	50	300	Characteristic and persistent odour. Turns violet on exposure. $FeCl_3$ and other oxidising agents give azure-blue precipitate.
Diphenylamine.	$(C_6H_5)_2.NH$	54	110	Nearly insoluble plates. Deep blue colour on adding to its solution in pure sulphuric acid a trace of nitrous sulphuric acid.
Para-amido-diphenyl-amine.	$C_6H_4(NH_2)C_6H_5.NH$	61	...	Small lustrous plates, becoming green in the air. $FeCl_3$ gives red colour, changing to green, and on concentration a green precipitate, soluble in H_2SO_4 with a carmine-red colour.
Paraphenylene-diamine. Paradiamido-benzene.	$C_6H_4:(NH_2)_2$	140	267	Sparingly soluble tablets. Oxidised to quinone by MnO_2 and dilute H_2SO_4.
Dimethyl-para-diamido-benzene.	$C_6H_4:\left\{\begin{matrix}NH_2\\N(CH_3)_2\end{matrix}\right.$	41	257	Easily soluble. Gives methylene blue with a solution of H_2S in hydrochloric acid. See page 211.
Para-amidophenol.	$C_6H_4(OH).NH_2^{p}$	184 decomposing.	...	Colourless plates, rapidly turning brown. Alkaline solution becomes violet on exposure, and yields quinone with oxidising agents. With bleaching solution, a violet-colour, changing to green.
α-Amido-alphanaphthol.	$C_{10}H_6(OH)^{a}.NH_2^{a}$	...	...	On agitating the alkaline solution with air, a dirty green colour is produced, changing to yellow. With bromine, water yellow-white crystalline precipitate. With oxidising agents yields the theoretical amount of α-naphthaquinone.
β-Amido-alphanaphthol.	$C_{10}H_6(OH)^{a}.NH_2^{\beta}$	...	...	On agitating the alkaline solution with air, permanent grass-green colour, and green scum soluble in alcohol to pure green solution. Br and $FeCl_3$ give yellowish or green precipitate, and no naphthaquinone is formed on heating.
Amido-resorcinol.	$C_6H_3(OH)_2.NH_2$	...	...	Flat plates turning green in the air. NaHO gives deep blue colour, changing to green and brown. $FeCl_3$ gives deep brown colour, and then nearly black precipitate.

ROSANILINE AND ITS ALLIES.

Rosaniline, a base of which the salts are usually known in commerce as fuchsine and magenta, was one of the first—and still is one of the most interesting and important—of the basic colouring matters obtained from coal-tar. It is the type of a large number of bodies, not a few of which are or have been of practical importance. Many of them dye silk and wool without the aid of a mordant, and by suitable means they can also be fixed on vegetable fibres.

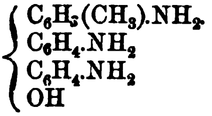
Rosaniline and its allies are derivatives of the hydrocarbon triphenylmethane, obtained by the action of benzene on chloroform, in presence of aluminium chloride:—$H.C\vdots Cl_3 + 3C_6H_5.H = 3HCl + (C_6H_5)_3\vdots C.H$. By oxidation of the hydrocarbon with chromic acid in glacial acetic acid solution at 100° C. (vol, ii. page 526), triphenyl-methyl alcohol or triphenyl carbinol, $(C_6H_5)_3C.OH$, is obtained. On the other hand, when slowly added to cold fuming nitric acid, triphenylmethane is converted into the trinitro-derivative, $(C_6H_4NO_2)_3CH$. This may be oxidised by treatment with chromic acid to the corresponding carbinol, $(C_6H_4NO_2)_3\vdots C.OH$, which when partially reduced by zinc-dust and acetic acid is converted into pararosaniline, $(C_6H_4NH_2)_3C.OH$. Hence, pararosaniline has the constitution of a triamidotriphenyl-carbinol, while its homologue rosaniline is methyl-pararosaniline or triamido-diphenyl-tolyl-carbinol.

Pararosaniline.



$$C\left\{\begin{array}{l} C_6H_4.NH_2 \\ C_6H_4.NH_2 \\ C_6H_4.NH_2 \\ OH \end{array}\right.$$

Rosaniline.



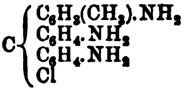
$$\left\{\begin{array}{l} C_6H_3(CH_3).NH_2 \\ C_6H_4.NH_2 \\ C_6H_4.NH_2 \\ OH \end{array}\right.$$

By the action of reducing agents the bases lose oxygen. Thus rosaniline yields leucaniline, $(C_7H_6NH_2)(C_6H_4NH_2)_2\vdots CH$, and pararosaniline the lower homologue triamido-triphenylmethane, $(C_6H_4NH_2)_3\vdots CH$. The salts of these bases are colourless.

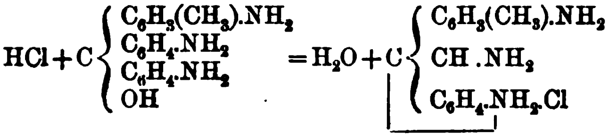
Pararosaniline and rosaniline are well-defined bases which react with acids to form salts, with elimination of the elements of water. Thus with hydrochloric acid, rosaniline reacts in the following manner:—$C_{20}H_{21}N_3O + HCl = C_{20}H_{19}N_3.HCl + H_2O$. In constitutional formulæ the reaction must be expressed as follows:[1]—

---

[1] The formula for rosaniline hydrochloride given in the text shows one nitrogen atom as exercising pentavalent functions, and is generally regarded as the most probable. An alternative view of the constitution of magenta is:—



$$C\left\{\begin{array}{l} C_6H_3(CH_3).NH_2 \\ C_6H_4.NH_2 \\ C_6H_4.NH_2 \\ Cl \end{array}\right.$$



$$HCl+C\left\{\begin{array}{l}C_6H_3(CH_3).NH_2\\C_6H_4.NH_2\\C_6H_4.NH_2\\OH\end{array}\right. =H_2O+C\left\{\begin{array}{l}C_6H_3(CH_3).NH_2\\CH\ .NH_2\\C_6H_4.NH_2.Cl\end{array}\right.$$

All the amido-derivatives of di- and triphenyl-carbinol react similarly with acids.

On account of this peculiar behaviour, the constitution of rosaniline and its allies was formerly misunderstood, but for representing many of their reactions the formulæ of the anhydrides may be conveniently used.

When a mixture of one molecule of para-toluidine with two of aniline is treated with an oxidising agent of moderate power, such as arsenic acid or mercuric chloride or nitrate, pararosaniline results; and when a molecule of ortho-toluidine is substituted for the second molecule of aniline, rosaniline is produced, according to the equation:—$CH_3^p.C_6H_4.NH_2+C_6H_5.NH_2+CH_3^o.C_6H_4.NH_2+O_3=C_{20}H_{21}N_3O+2H_2O$.

By treatment with nitrous acid, rosaniline and pararosaniline are converted into rosaurin and aurin respectively, while, on the other hand, by heating rosaurin and aurin to 120° with strong ammonia the reverse action occurs, and rosaniline and pararosaniline are respectively obtained (see page 161).

Rosaniline and pararosaniline are themselves colourless, but their salts are remarkable for the intense crimson-red colour of their solutions. Rosaniline hydrochloride forms the commercial dye known as *magenta* or *fuchsine;* while *acid magenta* is a mixture of the sodium salts of several rosaniline-sulphonic acids.

From the residues of the manufacture of rosaniline the less hydrogenised bases chrysaniline, $C_{19}H_{15}N_3$, and chrysotoluidine, $C_{20}H_{17}N_3$, are also obtainable. They are remarkable for forming almost insoluble nitrates, and the hydrochlorides constitute the commercial product known as *phosphine* or aniline orange. *Safranine* and the *indulines* are also secondary products of the manufacture of rosaniline.

By heating a salt of rosaniline with aniline, one, two, or three atoms of hydrogen in the original base may be replaced by the radical phenyl, with the formation of mono-, di-, or lastly, triphenylrosaniline, $C_{20}H_{18}(C_6H_5)_3N_3O$. These substituted products become more intensely blue with each replacement of the hydrogen atoms, so that the salts of the mono-derivative are reddish-violet, those of diphenyl-rosaniline bluish-violet, while the triphenylated base yields salts of a nearly pure blue (*Bleu de Paris*, page 224).

The dye known as *diphenylamine-blue* is of similar constitution to Paris blue, being the hydrochloride of triphenylpararosaniline. It is obtained by heating diphenylamine with oxalic acid: — $3(C_6H_5)_2NH+C_2H_2O_4=3H_2O+CO+C_{19}H_{14}(C_6H_5)_3N_3$. The dye *azuline*, obtained by heating aurin with aniline and benzoic acid, is apparently an impure kind of diphenylamine blue. By the action of methyl chloride or ethyl chloride on diphenylamine blue, or by using methyl- or ethyl-diphenylamine in the process of manufacture, substitution-products are obtained, the hydrochlorides of which are known in commerce as *methyl blue* and *ethyl blue*. They dye a purer blue shade than the unsubstituted diphenylamine blue. If a mixture of diphenylamine (phenylaniline) and phenyltoluidine (instead of the former base only) be heated with oxalic acid or carbon hexachloride, triphenylrosaniline, $C_{20}H_{16}(C_6H_5)_3N_3$, is obtained.

Just as several of the atoms of rosaniline and pararosaniline may be replaced by phenyl or tolyl, so may the radicals ethyl or methyl be substituted for one, two, or three atoms of the hydrogen in rosaniline. The replacement is effected by heating magenta or free rosaniline with alcoholic potash or soda and chloride or iodide of methyl. The *Hofmann's violets* so obtained range from RRR, the very red, which is chiefly a salt of monomethyl-rosaniline, $C_{20}H_{20}(CH_3)N_3O$, to BBB, the bluest shade, consisting of the highest substitution-products.[1] Similar, but not identical, dyes may be obtained by introducing the methyl or ethyl radical into aniline or diphenyl-amine before submitting the latter to the action of oxidising agents. *Methyl violet* is thus produced.

The colouring matter known as *malachite green* or benzaldehyde green differs from all the preceding in the fact that only two instead of all three of the phenyl groups of the triphenyl carbinol are amido-substituted. Thus malachite green is a salt of tetramethyl-diamido-triphenyl-carbinol, and *brilliant green*, *helvetia green*, *fast green*, and *resorcin purple* have an allied constitution.

Many of the basic colouring matters of the rosaniline group are convertible into more readily applicable dyes by sulphonation. The sulphonated dyes thus obtained are readily soluble, and dye silk and wool in acid baths. Usually they are not readily fixed on cotton, except *alkali blue*, in which the basic character of the Paris blue from which it is derived is not wholly destroyed by conversion into a mono-sulphonic acid.

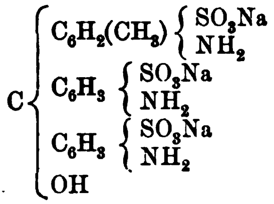
---

[1] It is a curious fact that while the substituted rosanilines become bluer with each replacement of the hydrogen atoms by phenyl, tolyl, methyl, or ethyl, the colour of the substituted *mauveines* follows the reverse rule.

In some cases, as in that of *acid magenta*, the sulphonated dye retains the hydroxyl group of the rosaniline from which it is derived, and hence is of the carbinol type. In other cases, as for instance in *alkali-blue*, the sulphonated dye appears to lose the elements of water, just as the basic dye does on combining with an acid. This is illustrated by the following examples, which suffice to indicate the formulæ of the whole class:—

Acid Magenta.

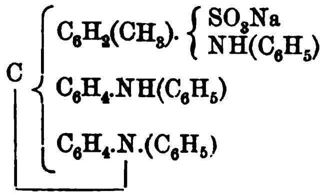
Sodium salt of Rosaniline-trisulphonic acid.[1]



$$C\begin{cases} C_6H_2(CH_3)\begin{cases}SO_3Na\\ NH_2\end{cases}\\ C_6H_3\begin{cases}SO_3Na\\ NH_2\end{cases}\\ C_6H_3\begin{cases}SO_3Na\\ NH_2\end{cases}\\ OH\end{cases}$$

Alkali Blue.

Sodium salt of Triphenyl-rosaniline-monosulphonic acid.



$$C\begin{cases} C_6H_2(CH_3).\begin{cases}SO_3Na\\ NH(C_6H_5)\end{cases}\\ C_6H_4.NH(C_6H_5)\\ C_6H_4.N.(C_6H_5)\end{cases}$$

The colouring matters of the rosaniline group may be conveniently classified as aniline red, aniline blues, aniline violets, aniline greens, and associated dyes. This arrangement will be adopted in their description.

Rosaniline. Aniline Red. Triamidotolyl-diphenyl-carbinol. $C_{20}H_{21}N_3O = (C_6H_4NH_2)_2(C_7H_6NH_2)COH$.

Rosaniline is the artificial organic base the salts of which form the magnificent dyeing materials known as *aniline-red*, *magenta*, *fuchsine*, *azaleine*, *rubine*, and by other more fanciful names. The colouring matter is produced whenever a mixture of aniline and toluidine is heated to about 180° C. with an oxidising agent of moderate power. A. W. Hofmann showed that the presence of both aniline and toluidine—which coexist in commercial aniline oils—was essential to the production of the colour, and represented the reaction thus:—$C_6H_7N + 2C_7H_9N + O_3 = C_{20}H_{19}N_3 + 3H_2O$. The more recent researches of E. & O. Fischer have shown that the free base contains oxygen, and on reacting with acids loses the elements of water (page 214).

A great number of methods of oxidising aniline oil for the production of rosaniline have been employed and patented, but only three are in general use, namely:—the arsenic acid, the mercuric nitrate, and the nitrobenzene processes.[2] According to the oxidising agent employed, and the subsequent treatment, the product may be the hydrochloride, nitrate, acetate, or other salt of rosaniline, but the first is now by far the most commonly met with.

---

[1] According to Benedikt, acid magenta is a mixture of the sodium salts of mono- and di-sulphonated rosaniline.

[2] According to the *arsenic acid process*, 100 parts of "aniline oil for red" are heated with 128 parts of arsenic acid of 75° Baumé for eight hours to a

Free rosaniline can be obtained by precipitating a solution of either of the commercial salts of rosaniline by excess of ammonia. If a boiling solution of the hydrochloride be employed, a reddish crystalline precipitate is produced, and the colourless liquid deposits on cooling a further crop of crystals of the pure base in colourless needles and plates, which have the composition $C_{20}H_{21}N_3O$ or $C_{20}H_{19}N_3,H_2O$.

Rosaniline is a non-volatile, colourless, bitter substance. Heated in boiling water it melts, and dissolves to the extent of 0·3 per cent., a portion being deposited on cooling. In alcohol it dissolves in the proportion of about 1 per cent. In ether, rosaniline dissolves to form a colourless solution, which dyes silk crimson, and gives a fine crimson colour on agitation with dilute acetic acid. In benzene, rosaniline is said to be insoluble, but it is very soluble in aniline.

temperature somewhat exceeding the boiling point of aniline, in a boiler fitted with a condensing tube. Water and a part of the aniline employed distil over. The residue is boiled with water, and the liquid filtered from the insoluble matter, which contains mauvaniline, violaniline, and some chrysaniline. The solution, which contains arseniate and arsenite of rosaniline, chrysaniline, excess of arsenic acid, and resinous substances, is treated with a large excess of common salt. Sodium arsenite and arseniate and rosaniline hydrochloride are formed, and the last of these, being sparingly soluble in strong brine, separates out. The precipitated colouring matter is dissolved in water and purified by crystallisation or again precipitated by the addition of salt. The mother-liquors yield an impure magenta, known as *cerise* or *geranium*. The arsenic is recovered by treating the waste-liquors with lime, when arsenite and arseniate of calcium are precipitated. The resinous matters may be used for the production of the colouring matters known as *grenadin* and *maroon*.

A very pure nitrate of rosaniline may be obtained by oxidising aniline oil with *mercuric nitrate*, and this may be converted into the hydrochloride by double decomposition with common salt.

Instead of using arsenic acid, *nitrobenzene* and ferrous chloride are sometimes employed. The latter body is oxidised by the nitrobenzene, and the product in turn oxidises the aniline, so that it acts as a carrier of oxygen. 100 parts of aniline oil are treated with two-thirds of the amount of hydrochloric acid required for neutralisation, and 50 parts of nitrobenzene added. The mixture is heated, while from 3 to 5 parts of iron filings are gradually added. The subsequent operations are the same as in the arsenic acid process. The bye-products contain much induline, but no chrysaniline.

A valuable article on the manufacture of magenta has been published by P. Schoop in *Dingler's Polytechnische Journal*, cclviii. 276, and translated in *Jour. Soc. Dyers, &c.*, ii. 118.

Rosaniline loses no water at 100° C. When heated alone to about 130°, it is decomposed. If the free base or one of its salts be heated with water under pressure to about 240° C., phenol and ammonia are produced, with other products; but if the water be acidulated with hydrochloric acid, or if the rosaniline be heated with concentrated hydriodic acid, it is completely resolved into aniline and toluidine.

SALTS OF ROSANILINE. Rosaniline is a well-defined and powerful base, capable of combining with either one, two, or three equivalents of an acid. The tri-acid salts are brownish-yellow, both in the solid state and in solution, and are readily soluble in water and alcohol. The di-acid salts are little known and difficult to prepare. The mono-acid salts, typified by ordinary *magenta*, are the most interesting and important. They are stable crystalline bodies having a beetle-green metallic lustre, and are mostly soluble in water and alcohol, forming violet-red, non-fluorescent solutions of high tinctorial power. Their solutions dye silk and wool a magnificent crimson colour, without the aid of a mordant, and by proper means the colour may be fixed on vegetable fibres. Formerly, English-made *magenta* was generally rosaniline acetate; the French article known as *roseine* consisted of the hydrochloride; while the nitrate was known as *rubine* or *azaleine*.

Rosaniline Acetate, $C_{20}H_{19}N_3,C_2H_4O_2$, forms magnificent crystals with a beetle-green reflection, which are apt to turn brownish-red. It is one of the soluble of the salts of rosaniline, and also dissolves freely in alcohol. The acetate was formerly the most commonly occurring salt of rosaniline, but latterly has been superseded by the hydrochloride.

Rosaniline Chromate is a brick-red, nearly insoluble powder.

Rosaniline Hydrochloride, or Hydrochlorate of Rosaniline, $C_{20}H_{19}N_3,HCl$. This compound, which constitutes the ordinary *magenta*, *fuchsine*, or *roseine* of commerce, crystallises in very small, deliquescent rhombic plates, which are somewhat sparingly soluble in pure water, but more readily in acidulated water and in alcohol. It is also soluble in amylic alcohol, but insoluble in ether. Rosaniline hydrochloride combines with platinic chloride to form an uncrystallisable chloroplatinate. With concentrated hydrochloric acid, rosaniline hydrochloride yields brown needles of the triacid salt, $C_{20}H_{19}N_3,3HCl$. This body dissolves in a little water with brown colour, but on dilution splits up into hydrochloric acid and the mono-acid salt, the re-formation of which is indicated by the change of the colour of the solution to crimson.

Rosaniline Nitrate, $C_{20}H_{19}N_3,HNO_3$, constitutes the commercial products known as *azaleine* and *rubine*. It is not often met with.

Rosaniline Picrate forms magnificent reddish needles, nearly insoluble in water.

Rosaniline Sulphate much resembles the hydrochloride.

Rosaniline Tannate has a practical importance in dyeing, as its insolubility in water affords a means of fixing the colouring matter on vegetable fibres, and of recovering rosaniline from spent dye-liquors. It dissolves in alcohol, wood spirit, and acetic acid.

MAGENTA. FUCHSINE. ANILINE RED. These names, as also *rubeine*, *roseine*, *azaleine*, &c., are used to signify the salts of rosaniline as occurring in commerce. Formerly, the English-made product generally consisted of rosaniline acetate, and was known as *magenta;* the French article called *roseine* consisted of the hydrochloride; while the nitrate was known as *rubeine* or *azaleine*.[1] Now the hydrochloride has to a great extent superseded the acetate and nitrate of rosaniline, and the distinction is no longer observed. The following reactions are common to all the commercial varieties of magenta.

Magenta usually occurs in beetle-green crystals or as a dark-green crystalline powder. It dissolves in water with magnificent crimson colour without fluorescence. The dilute aqueous and alcoholic solutions of magenta exhibit characteristic absorption-spectra, having a well-defined black band between the Fraunhöfer lines D and E.

Solutions of magenta dye silk and wool without a mordant. The colouring matter is partially removed by boiling water, while soap removes it completely.

Caustic alkalies, ammonia, baryta, lime, and magnesia decompose solutions of magenta, free rosaniline being precipitated in a crystalline and nearly colourless state. If magnesia be used,[2] and the operation conducted in a boiling hot liquid, so that some of the liberated rosaniline may remain in solution, and the liquid be then filtered out of contact with air, a colourless filtrate is obtained. On passing carbon dioxide, or the air exhaled from the lungs, through this colourless solution of rosaniline, a crimson coloration is produced, owing to the formation of rosaniline carbonate. The reaction constitutes a delicate test for carbon dioxide.

---

[1] *Magenta-violet* or *fuchsine V* is a mixture of rosaniline and mauvaniline hydrochlorides.

Cerise is a colouring matter containing magenta, and is used in dyeing browns. The mother-liquors from which magenta has been salted out contain phosphine, unprecipitated magenta, and a brown colouring matter. They are treated with milk of lime, and the precipitate separated, dissolved in acidulated water, and salted out. The cerise obtained forms an amorphous brown mass, with a vitreous fracture.

Maroon and *grenadin* are brown colouring matters obtained by purifying the resinous matters formed in the manufacture of magenta.

Cardinal and *amaranth* consist of mixtures containing magenta as the chief constituent.

[2] If one of the other bases mentioned in the text be substituted for magnesia, it should be added gradually, and only in sufficient quantity to effect exact decomposition, as indicated by the decolorisation of the solution.

If a solution of magenta be treated with excess of soda or ammonia and then agitated with ether, the liberated rosaniline dissolves. The separated ethereal solution is colourless, but dyes silk a fine crimson, and on shaking with dilute acetic acid yields a crimson solution.

Excess of strong hydrochloric acid turns magenta solutions yellow or brown, owing to the formation of a triacid salt, which is decomposed on copious dilution, or on adding a solution of sodium acetate, with restoration of the original crimson colour.

Reducing agents, such as zinc and acetic or hydrochloric acid, stannous chloride, sulphurous acid, &c., decolorise solutions of magenta with formation of colourless salts of leucaniline, $C_{20}H_{21}N_3$. This base differs from the products resulting from the reduction of safranine, magdala-red, and certain other colouring matters, in not being reconverted into rosaniline by atmospheric oxygen. On the other hand, oxidation of leucaniline to rosaniline can be effected by manganese dioxide, chloranil, and similar agents.

Strong oxidising agents, such as permanganates, hypochlorites, and chlorine, decolorise solutions of magenta. Oxidising agents of moderate power produce new colouring matters, a yellowish-red product known as *aniline-scarlet* being formed by the action of hydrogen peroxide or lead nitrate. Chromic acid acts on magenta with formation of a brown colouring matter.

Aldehyde and alcoholic solution of shellac convert magenta into blue colouring matters.

Solid magenta dissolves in strong sulphuric acid with yellowish-brown colour, becoming violet-red on dilution with water.

Detection of Magenta. When perfectly pure, magenta is not poisonous, but as occurring in commerce it frequently contains arsenic, and hence is unsuitable for colouring confectionery, syrups, wine, &c. Its use for such purposes is absolutely forbidden in some countries.

The detection of magenta is based on the foregoing reactions, but in order to apply these satisfactorily it is usually necessary to isolate the colouring matter more or less perfectly.

For the detection of magenta in *wine* or other coloured liquids,[1] about 50 c.c. of the sample should be treated with excess of baryta water, heated to boiling, and filtered. The filtered liquid is then cooled and shaken with ether, which will take up the rosaniline. The ethereal solution, though colourless or nearly so, will communicate a violet-red colour to dilute acetic acid, and the resultant solution will exhibit a characteristic absorption-spectrum.[1] On evaporation to dryness, the ethereal solution will yield a residue soluble in strong hydrochloric acid with yellow-brown colour, changed to violet-red on dilution, and permanently decolorised by warming with zinc. If a thread of white silk or wool be placed in the ethereal solution, and the ether allowed to evaporate, the rosaniline will be taken up by the fibre, which will acquire a crimson colour when moistened with dilute acetic acid. A fairly approximate colorimetric determination of the magenta present may be obtained by comparing the tint with those of standard specimens of wool or silk prepared in a similar manner with known quantities of the colouring matter.

---

[1] The froth of wine coloured with magenta has a distinct violet tint.

A modification of the above test consists in rendering 50 c.c. of the wine slightly alkaline with ammonia and boiling the liquid with a little white wool till all the alcohol and ammonia are expelled. The wool is then removed, washed with water, and at once heated with a few drops of caustic soda solution till dissolved. After cooling, about 5 c.c. of water and the same measure of alcohol are added, and the liquid is shaken up with 10 c.c. of ether. The ethereal solution is then separated, and examined as already described.

An alternative process for the detection of magenta in wine is to warm 50 c.c. with a strong solution of lead acetate, filter, and add one drop of acetic acid to the filtrate. This is next shaken with 10 c.c. of amylic alcohol, which will remain colourless if the wine be pure, but will be coloured red in the presence of *magenta*, red-violet by *archil*, and yellow by *rosolic acid.* If the amylic alcohol be separated and agitated with dilute ammonia, it will be decolorised, the ammoniacal liquid acquiring a bluish-violet colour if archil and a red-violet if rosolic acid be present, while magenta communicates no marked colour to the ammonia.

Of late years, the use of ordinary magenta for colouring wine has been to a great extent superseded by that of other coal-tar dyes, especially the sulphonated rosaniline known as *acid magenta* (page 226). To detect this colouring matter, J. Herz (*Analyst*, xi. 175) recommends that from 30 to 50 c.c. of the wine, or preferably 100 c.c. previously concentrated to that volume, should be treated with half its measure of a cold saturated solution of magnesium sulphate, and then from 10 to 20 c.c. of a strong solution of caustic soda stirred in. The precipitate of magnesium hydroxide carries down with it all the natural colouring matter of the wine, and also most of the artificial colouring matters, except archil and sulphonated magenta. If the filtrate be not colourless, or at most merely yellowish-red, the treatment with magnesium sulphate and soda should be repeated. A colourless or yellowish filtrate having been obtained, it is acidulated with dilute sulphuric acid, when if acid magenta or other sulphonated dye be present the liquid will re-acquire its original violet-red colour, and from the depth of the tint an approximate estimate of the amount present can be made. If archil be present, the alkaline filtrate will be bluish, becoming litmus-red on addition of acid. If the excess of acid be nearly neutralised, and the coloured liquid be shaken for some minutes with peroxide of lead and filtered, a colourless filtrate will be obtained if the previous coloration was due to *archil*, while in the case of the *acid magenta* the red colour remains, and its intensity indicates the amount of the dye present.

---

[1] In the Paris Municipal Laboratory, where a large number of wines are examined, it is usual to test for *basic* coal-tar dyes, including ordinary magenta, by adding enough baryta water to render the wine slightly alkaline, and then shaking with amylic alcohol or acetic ether. The upper layer, either immediately or after acidulation with acetic acid, will be coloured if a basic dye be present.

The gelatinous precipitate of magnesium hydroxide is next stirred up with hot water, and the liquid separated by decantation or filtration.[1] The precipitate is then mixed with sand, dried at 100°, and exhausted with ether. The ethereal solution will contain any ordinary magenta present in the original wine, and can be examined in the manner already described (page 222). Herz mentions a dye called *cassissine* which is extracted together with the ordinary magenta, but dyes wool reddish-brown and is left as a reddish-brown residue on evaporating the ethereal solution. The dyed wool becomes yellow when treated with strong hydrochloric acid, and colourless on adding ammonia.

---

[1] If only the natural colouring matter of the wine be present, or *bilberry* has been used, this liquid is yellowish-brown; with *archil*, dark violet; with *ponceau*, onion or ponceau red; with *cassissine*, pale red or dark yellow; and with *vinicoline bordelaise*, yellowish-red or reddish-brown, giving a violet zone when poured on the surface of strong sulphuric acid. This last colouring matter is said to be a mixture of Biebrich red and elderberry extract. If the coloured liquid be agitated with amylic alcohol, and the solution so obtained evaporated, the residue will be dark grey or brownish-grey if only natural or vegetable colouring matters are present; violet in presence of *archil;* dirty white with either ordinary or acid magenta; dirty yellow-brown with *cassissine;* and crimson-red with *vinicoline*.

To detect magenta in wine, R. Kayser (*Jour. Soc. Chem. Ind.*; iv. 291) recommends that 100 c.c. of the sample should be shaken with 20 c.c. of colourless amylic alcohol. The liquid is then diluted with water and the amylic alcohol layer examined with a spectroscope. If the characteristic absorption-bands of magenta are observed, another portion of the sample should be treated with excess of ammonia, and shaken with amylic alcohol as before, which will be coloured red by ordinary magenta, while sulphonated magenta is not extracted from alkaline liquids.[1]

In the Paris Municipal Laboratory, for the detection of *acid dyes* in wine, 10 c.c. of the sample is rendered strongly alkaline by the addition of 2 to 3 c.c. of a 5 per cent. solution of caustic potash; from 2 to 3 c.c. of a 20 per cent. solution of mercuric acetate is next added, and the whole well shaken and filtered. With pure wine, the filtrate is colourless, and remains so even after acidulation with hydrochloric acid, but will be yellow or red if acid magenta or other sulphonated coal-tar dye be present.

Further information respecting the detection of foreign colouring matters in wine will be found in vol. i. pages 86 to 88.

The methods already described for the detection of magenta in wine are applicable to other articles coloured by it.

The detection of magenta on fibres dyed with it presents no difficulty. The colour is destroyed by sodium sulphide, owing to its reduction to leucaniline. Alkalies also bleach the colour from liberation of rosaniline, which may be extracted by ether (see page

---

[1] It is not evident why free rosaniline should colour amylic alcohol as stated. There is also a discrepancy between this process and the experience of J. Herz, who does not appear to have observed the extraction of either ordinary or acid magenta from acid solutions by treatment with amylic alcohol. On the contrary, he finds that the colour of the wine after the treatment is cherry-red in the presence of *ordinary magenta*, reddish-violet with *acid magenta*, dark cherry-red with *Bordeaux B*; and yellowish-red with *ponceau RRR*. On evaporating the amylic alcohol solution to dryness and testing the residue with reagents, Herz observed the following reactions :—

Colouring Matter.	Residue from Amylic Alcohol.			
	Colour.	With Concent. H_2SO_4.	With Concent. HCl.	With Caustic Soda.
Archil.	Violet-red.	Blue.	Red.	Blue.
Bordeaux B.	Carmine.	Carmine.	Carmine.	Carmine.
Ponceau R.R.R.	Dark-red.	Crimson.	Crimson.	Brown.
Cassissine.	Violet-purple.	Yellow.	Yellowish-brown.	Red.
Vinicoline Bordelaise.	Cherry-red.	Brown.	Red.	Brown.

222). Strong hydrochloric acid turns the fabric yellow or brown, the colour being restored by copious dilution.

Liebmann and Studer (*Jour. Soc. Chem. Ind.*, v. 288) recommend that 100 c.c. of the wine should be evaporated to about 10 c.c., saturated with sulphur dioxide, and then precipitated with lead acetate. To the filtered liquid a drop of aldehyde or acetone is added, when a violet coloration will be produced if magenta or acid magenta be present even in the proportion of one milligramme per litre. The test is equally applicable to syrups, lozenges, &c. The treatment with lead acetate is not essential. A similar method may be employed for the detection of magenta in cudbear and archil.

In testing wine for magenta it should always be borne in mind that the colouring matter is precipitated by tannin, and hence is often present most largely in the deposit, from which it be extracted by treatment with an alkali and agitation with ether.

EXAMINATION OF COMMERCIAL MAGENTA. Pure magenta consists simply of the hydrochloride or other salt of rosaniline, mixed with more or less of the corresponding compound of pararosaniline. The commercial product generally contains, in addition, more or less water, mineral impurities, resinous substances, and, if prepared by the arsenic acid process, a notable quantity of arsenic. Besides these impurities, actual adulterants are sometimes present, the most usual being sugar, starch, dextrin, sodium sulphate, and occasionally bronze powder.

Magenta of good quality being generally well crystallised, powdered or imperfectly crystalline specimens are always open to suspicion.

The blue shades of magenta are generally the purest. The yellow shades, if made by the arsenic acid process, usually contain *phosphine;* magenta made by the nitrobenzene process contains no phosphine.

A solution of pure magenta is entirely decolorised by sulphurous acid, while impure samples are turned yellow or brown; or the hot aqueous solution of the sample may be treated with hydrochloric acid, and zinc-dust then gradually added in small quantities at a time, till the red colour is destroyed. With pure magenta the reduced liquid will be colourless, but if *chrysaniline* be present it will have a yellow tint.

Arsenic is sometimes present in commercial magenta in considerable proportion, as much as 6½ per cent. having been met with. It may be detected by Marsh's test. For its determination, the acidulated solution may be treated with bromine water, excess of ammonia added, the liquid filtered if necessary, and magnesia mixture then added. A precipitate of the ammonio-magnesium arseniate, deposited in streaks in the track of the glass rod used for stirring, will be gradually formed if arsenic be present. The arseniate may be distinguished from the similar phosphate by washing the precipitate or streaks with water, and adding silver nitrate, when the arseniate will be turned brown, or the phosphate yellow.

The detection of other impurities and adulterants of magenta will be described in the section on the "Examination of Commercial Colouring Matters."

ACID MAGENTA (page 217), called also *magenta S* and *rubine S*, is obtained by heating ordinary magenta with fuming sulphuric acid or sulphonic chloride, SO_3HCl. The product is poured into water, neutralised with milk of lime, the solution filtered from the calcium sulphate, and the filtrate decomposed by sodium carbonate. The calcium carbonate is filtered off and the filtrate evaporated to dryness. Acid magenta occurs in grains or powder of a green colour and metallic lustre. It dissolves readily in water, forming a bluish-red solution, which is nearly decolorised by alkalies without a precipitate being formed, and nothing is yielded to ether. Dilute acids, even carbonic acid, restore the colour, which is not materially altered by a considerable excess. In strong sulphuric acid, the solid dye dissolves with yellow colour, becoming gradually red on dilution.

According to C. Blarez, all red coal-tar dyes except acid magenta, and also all red vegetable colouring matters, are completely decolorised when their aqueous solutions are slightly acidulated with tartaric acid and digested with dioxide of lead.

In its behaviour with reducing agents and acetone, acid magenta reacts like the basic dye.

Acid magenta is employed for colouring red wines. Being insoluble in ether, either in acid or alkaline liquids, it may be distinguished from ordinary magenta, and may be more definitely recognised as described on page 223.

Acid magenta has only about half the dyeing power of ordinary magenta, but can be dyed from strongly acid baths, and hence is conveniently employed in conjunction with acid yellow, indigo-carmine, &c.

On the fibre, acid magenta is unaffected in colour by a mixture of equal measures of hydrochloric acid and water, whereas ordinary magenta is turned yellow or brown. The reagent dissolves some of the acid magenta, and acquires a cherry-red colour.

Aniline Blues.

As stated already (page 215), the phenylated derivatives of rosaniline and pararosaniline dye bluer shades than the unsubstituted bases, and this in proportion to the number of hydrogen atoms replaced by phenyl, C_6H_5. Thus the colouring matter known as *regina violet* (page 233) is chiefly a salt of diphenylrosaniline, while the various commercial aniline blues are mostly triphenylated derivatives; and Benedikt states that hexaphenylrosaniline yields a purer blue than any other colouring matter known.

Besides a few aniline colours of a somewhat different constitution, there occur in commerce two parallel series of blue dyes, which are triphenylated derivatives of pararosaniline and rosaniline respectively. Thus:—

	Triphenyl-pararosaniline. $C\left\{\begin{matrix}C_6H_4.NH(C_6H_5)\\ C_6H_4.NH(C_6H_5)\\ C_6H_4.NH(C_6H_5)\\ OH\end{matrix}\right.$	**Triphenyl-rosaniline.** $C\left\{\begin{matrix}C_6H_3(CH_3).NH(C_6H_5)\\ C_6H_4.NH(C_6H_5)\\ C_6H_4.NH(C_6H_5)\\ OH\end{matrix}\right.$
Hydrochloride.	**Diphenylamine blue. Pararosaniline blue.**	**Rosaniline blue. Aniline blue. Spirit blue. Paris blue.**
Sodium monosulphonate.	**Alkali blue D. Soluble Diphenylamine blue.**	**Alkali blue. Soluble blue. Nicholson's blue.**
Sodium disulphonate.	**Bavarian blue DSF.**	**Silk blue.**
Sodium trisulphonate.	**Methyl blue BI for cotton. Bavarian blue DEF.**	**Soluble blue. China blue. Cotton blue. Opal blue. Water blue O or 6 B extra.**

The parallel compounds from para-rosaniline and rosaniline present a close analytical and general resemblance. In addition, the phenylated products from commercial rosaniline invariably contain more or less of their lower homologues (from para-rosaniline), and hence there is no sharp distinction between the two series of dyes.

DIPHENYLAMINE BLUE or Para-rosaniline Blue is the hydrochloride of triphenyl-pararosaniline, and contains $C_{19}H_{14}(C_6H_5)_3N_3.HCl$. It is prepared by heating diphenylamine, $(C_6H_5)_2:NH$, to 120°–130° with oxalic acid. The excess of oxalic acid is removed by washing with water, and unaltered diphenylamine by boiling with benzene, the residue being then converted into the hydrochloride. The commercial dye forms a brownish powder, having an odour resembling that of diphenylamine. It is insoluble in water, and only sparingly soluble in cold alcohol, but dissolves more readily on heating. The solution is turned greenish by hydrochloric acid. A two per cent. solution of the colouring matter in methylated spirit is employed to produce light and very pure shades of blue on silk. Diphenylamine blue dissolves in strong sulphuric acid with brownish-yellow colour, a blue precipitate being produced on dilution.

The colouring matter known as *azuline* or *azurine* is an impure hydrochloride of triphenyl-pararosaniline.

Colouring matters known as *methyl blue* and *ethyl blue* are obtainable by the action of methyl or ethyl chloride on diphenylamine blue; or by heating methyl- or ethyl-diphenylamine with oxalic acid. The products dye silk a still purer blue than that produced by diphenylamine blue. One of the purest blues is obtained by treating methyl-diphenylamine at 100° with chloranil (tetrachlorquinone), $C_6Cl_4O_2$,[1] and then further heating to 130°. The product is reduced to powder, washed with hydrochloric acid, dissolved in alcohol, and precipitated by water.

ROSANILINE BLUE, also called *Spirit Blue* or *Paris Blue*, is a salt of triphenyl-rosaniline, containing more or less of the corresponding salt of triphenyl-pararosaniline. To prepare it, rosaniline (prepared by precipitating a solution of the purest bluish magenta with ammonia or lime) is heated to about 180° with ten times its weight of aniline and some benzoic acid. The excess of aniline, together with the ammonia formed in the reaction, distils over. The product is neutralised with dilute hydrochloric acid, when aniline hydrochloride dissolves and the salt of the new base remains insoluble. This is washed first with dilute hydrochloric acid and then with water, and dried and powdered.[2]

The most usual form of occurrence of triphenylrosaniline is as the hydrochloride, $C_{20}H_{16}(C_6H_5)_3N_3.HCl$, but the sulphate and acetate are also met with. The first salt forms a greyish-green or brownish powder, which becomes pure blue at 100°; the sulphate and acetate bluish-violet, lustreless powders. In cold water the salts of triphenylrosaniline are quite insoluble, and nearly so in hot. In alcohol the acetate dissolves easily, and the hydrochloride and sulphate with more difficulty, to form deep blue solutions, unchanged or turned greenish by hydrochloric acid, and in which stannous chloride produces a blue precipitate. A cold alcoholic solution of spirit blue becomes brownish-red with soda or ammonia, but at a boiling heat a colourless solution is produced, and on dilution with water this yields a white precipitate of free triphenylrosaniline, $C_{20}H_{17}(C_6H_5)_3N_3.OH$, which rapidly becomes blue in the air. In concentrated sulphuric acid, spirit blue dissolves with brownish-yellow colour, and on dilution with water a blue precipitate is produced.

---

[1] Prepared by the action of potassium chlorate and hydrochloric acid on phenol.

[2] The blue obtained from rosaniline, as described in the text, is of a lower price and quality than diphenylamine blue. The less pure products have a reddish shade, especially observable in artificial light. The best qualities appear pure blue by gas or lamp light, and are sometimes known as *blue de nuit* and *bleu lumière*, but must not be confused with the *night blue* described on page 232. These qualities are also known as *spirit-blue 5B* and *6B*, the redder shades being described as *2B*, *3B*, &c., according to their quality. Spirit-blue is sometimes further purified by dissolving it in aniline and precipitating by hydrochloric acid, and by other methods. Such purified products are known as *opal blue* or *basic blue*.

Spirit blue is employed to produce bright blues on wool. The articles are dyed in a bath containing alum, sulphuric acid, or stannic chloride. Fibres dyed with spirit blue are nearly decolorised by hydrochloric acid, turned greyish-violet by soda, and changed to light blue, fading to colourless, by ammonia. Alcohol strips the fibre even in the cold.

SULPHONATED ANILINE BLUES.

Diphenylamine blue and spirit blue being insoluble in water, their practical application is attended with some inconvenience, to obviate which they are frequently sulphonated, with production of soluble colouring matters known as *soluble blue*, *water blue*, &c. (see page 224).

The greater the number of SO_3H groups that are introduced into triphenylrosaniline or its homologues, the more readily soluble the products become, but their fastness to light and air, soap, and alkalies decreases in the same proportion. Hence the higher sulphonic acids, such as triphenyl-rosaniline tetrasulphonic acid, are never prepared.

The sulphonated aniline blues are prepared by heating diphenylamine blue and spirit blue with concentrated sulphuric acid, the extent of the sulphonation depending on the proportion of acid used and the temperature employed. A soluble diphenylamine blue may be prepared directly by heating diphenylamine-sulphonic acid with oxalic acid, instead of sulphonating the previously prepared triphenylpararosaniline.

TRIPHENYLROSANILINE-MONOSULPHONIC ACID has the formula $C_{20}H_{15}(SO_3H)(C_6H_5)_3N_3$, and is formed by dissolving spirit blue in strong sulphuric acid and heating the solution to 30°–35° C. for five or six hours. On pouring the resultant brownish-yellow solution into water, the sulphonic acid is obtained as a bulky blue precipitate, which after being dried at 100° forms small grains having a metallic lustre. Its alkali-metal salts are soluble in water, but those formed with the heavy metals and alkaline-earth metals are insoluble or nearly so. By digesting the washed sulphonic acid in a quantity of caustic soda solution somewhat less than that required to combine with it, and filtering, a solution of the sodium salt is obtained, from which the solid compound may be prepared by saturating the liquid with common salt, or evaporating it to dryness with addition of a little ammonium carbonate.

Sodium triphenylrosaniline-monosulphonate forms the commercial dye-stuff known as *Nicholson's blue, alkali blue,* or *soluble blue.* It occurs in lumps or powder of a greyish, brownish, or dull blue colour. It dissolves readily in hot water, with light brown or bluish colour, which becomes deep blue on adding acetic acid, and on boiling the acidulated liquid the free sulphonic acid separates as a blue precipitate. Hydrochloric acid produces the same reaction in the cold, and on filtering a colourless liquid is obtained, unless a di- or trisulphonate be present. Caustic soda turns the solution of soluble blue reddish-violet, the colour changing on boiling to reddish-brown. Excess of ammonia decolorises the solution. Calcium chloride and stannous chloride produce blue precipitates. Soluble blue dissolves in strong sulphuric acid with fine brownish-red colour, becoming blue on dilution with water.

If wool be immersed in a hot solution of alkali blue, preferably containing borax, sodium silicate, sodium carbonate, or ammonia, the nearly colourless salt is taken up by the fibre and cannot be removed by washing with water; but on subsequently immersing the fibre in dilute sulphuric acid the blue colour is developed.

Cold alcohol readily removes the colour from wool or silk dyed with alkali blue. Caustic soda turns the fibre a yellowish-brown, while ammonia immediately destroys the colour. Hydrochloric acid nearly decolorises the fibre, and an acid solution of stannous chloride destroys it gradually.

Commercial alkali blue is liable to contain various impurities and adulterations. It should dissolve without residue in about five parts of hot water. Sugar, starch, and dextrin are sometimes added, and a considerable proportion of sodium carbonate, sulphate, or chloride is often present. Arsenic is not an unusual contamination. Alcohol dissolves the dye and leaves sodium sulphate and carbonate insoluble. The dye may be precipitated by saturating the aqueous solution with purified common salt, while sodium carbonate and sulphate remain in solution. The sulphate of sodium contained in the residue left on ignition represents that formed from the sulphonate, as well as that pre-existing as sulphate. Pure sodium triphenylrosaniline-monosulphonate will yield 22·6 per cent. of Na_2SO_4 on fusion with sodium carbonate and nitre. On ignition alone a low result is obtained, the sodium present being insufficient to fix all the sulphur, besides which more or less sulphide and sulphite will probably be formed.

Sodium triphenylpararosaniline-monosulphonate is known in commerce as *alkali blue D.* In its reactions it closely resembles its homologue from rosaniline, but is nearly insoluble in cold water, and in hot water forms a blue solution which has an odour of diphenylamine.

TRIPHENYLROSANILINE-DISULPHONIC ACID, having the formula $C_{20}H_{14}(SO_3H)_2(C_6H_5)_3N_3$, is obtained, together with the trisulphonic acid, when triphenylrosaniline hydrochloride (spirit blue) is digested with 4 or 5 parts strong sulphuric acid at 60° C. for five or six hours, and the temperature finally increased to 100°–110°. If the product be diluted with three or four times the quantity of water both sulphonic acids are precipitated, but if a comparatively large quantity of water be used the precipitate consists mainly of the disulphonic acid, while the trisulphonic acid dissolves and may be obtained as a blue precipitate by treating the filtrate with common salt or hydrochloric acid in excess. Triphenylrosaniline-disulphonic acid is slightly soluble in water, but insoluble in acid liquids, and hence is thrown down as a blue precipitate on acidulating the solution of one of its salts. Excess of soda turns the solution of its salts yellow. The sodium salt occurs in commerce under the name of *silk blue,* and *Bavarian blue DSF* consists principally of the corresponding derivative of pararosaniline, while *Blackley blue* is the sodium salt of diphenyl-tolyl-rosaniline-disulphonic acid.

TRIPHENYLROSANILINE-TRISULPHONIC ACID, of the composition $C_{20}H_{13}(SO_3Na)_3(C_6H_5)_3N_3$, is obtained as indicated above. It is soluble in water and alcohol. The *sodium, ammonium,* and *calcium salts,* mixed with more or less of the corresponding disulphonates, form the commercial colouring matters known as *water blue, cotton blue,* &c. (page 227). The ammonium salt forms dark lumps or grains having a coppery lustre; the sodium salt usually occurs as dark blue irregular lumps. *China blue* is a very porous variety of water blue, obtained by adding carbonate of ammonium to a very concentrated and slightly acid solution of the colouring matter.

Water blue is more soluble than alkali blue, and crystallises from its concentrated hot solution in flakes having a metallic lustre. Its solution is not completely precipitated by hydrochloric acid, under any circumstances; and not at all unless a large excess of the reagent be used or disulphonate be present. Caustic soda decolorises the solution or turns it reddish-brown. Water blue dissolves in strong sulphuric acid with dark yellowish-red colour, and on dilution a blue solution is formed, sometimes accompanied by partial precipitation.

Water blue differs from alkali blue in not being taken up by wool from an alkaline solution, and hence the fibre so treated is not rendered blue by subsequent immersion in dilute acid.

Strong sulphuric acid dissolves water blue from fibres dyed with it, with blue coloration, and a hydrochloric acid solution of stannous chloride behaves similarly. Caustic soda turns the fibre reddish-brown, and ammonia decolorises it immediately. Alcohol has no effect on the dyed fibre, even when boiling.

Water blue is chiefly used for dyeing cotton, being fixed by means of tannin, or by alizarin oil in conjunction with aluminium, antimony, or tin compounds. It is dyed on silk and wool in an acid bath, and in this case is always used in conjunction with other colouring matters.

The colouring matters known as *Bavarian blue DBF*, *methyl-blue M*, *BI for cotton*, &c., chiefly consist of the sodium salt of *triphenyl-pararosaniline-trisulphonic acid*, and closely resemble the homologue, ordinary water blue.

BLUES FROM TETRAMETHYL-DIAMIDO-BENZOPHENONE.

Several interesting colouring matters are obtainable by the

	Victoria Blue B.	Victoria Blue 4 R.	Night Blue.
Formula.	$C\left\{\begin{array}{l}C_6H_4.N(CH_3)_2\\C_6H_4.N(CH_3)_2\\C_{10}H_6{}^{\alpha}.NH(C_6H_5).Cl\end{array}\right.$	$C\left\{\begin{array}{l}C_6H_4.N(CH_3)_2\\C_6H_4.N(CH_3)_2\\C_{10}H_4{}^{\alpha}.N(CH_3)(C_6H_5).Cl\end{array}\right.$	$C\left\{\begin{array}{l}C_6H_4.N(CH_3)_2\\C_6H_4.N(CH_3)_2\\C_{10}H_6{}^{\alpha}.NH(C_7H_7).Cl\end{array}\right.$
Chemical nature.	Hydrochloride of Tetramethyl-phenyl-triamido-α-naphthyl-diphenyl-carbinol.	Hydrochloride of Pentamethyl-phenyl-triamido-α-naphthyl - diphenyl-carbinol.	Hydrochloride of Tetramethyl-tolyl-triamido-α-naphthyl-diphenyl-carbinol.
Physical characters.	Blue crystalline grains or powder with bronze reflection.	Bronze powder.	Brown-violet powder with bronze reflection.
Solubility in water.	Sparingly in cold, readily in hot, to blue solution, gradually depositing reddish resinous precipitate of free base on boiling. (Decomposition prevented by acetic acid.)	Soluble on heating to a bluish-violet solution.	Soluble with fine blue colour, becoming turbid and precipitated by boiling.
Hydrochloric acid to aqueous solution.	Green precipitate, changing to dark yellowish-brown; original colour restored on neutralising.	Same reaction as Victoria blue B.	Same reaction as Victoria blue B.
Caustic soda to aqueous solution.	Dark reddish-brown precipitate.	Violet-brown precipitate.	Pale reddish-brown precipitate.
Solid dye with strong sulphuric acid.	Reddish-yellow or reddish-brown; on dilution, yellow; and on adding more water, green and blue.	Yellowish-brown; on dilution, green and blue.	Orange solution; on dilution, blue, especially if nearly neutralised.

reaction of tetramethyl-diamido-benzophenone on phenyl-alpha-naphthylamine and its homologues in presence of condensing agents. Although the mode of preparation of these dyes is entirely different from that of diphenylamine blue and rosaniline blue, the products bear a certain constitutional relationship to these products. The preceding table (page 232) shows the composition and characters of the three chief members of the group.

Victoria and night blues dye wool and silk in a bath acidulated with acetic acid. Cotton is first mordanted with alizarin oil and aluminium acetate. Sulphuric acid changes the colour of the fibre to orange or reddish-brown, but the original blue colour is restored by washing.

Aniline Violets.

By the substitution, partial or complete, of the hydrogen of the NH_2 groups of rosaniline and pararosaniline by methyl or ethyl, various violet colouring matters are obtained, those compounds in which the substitution is carried furthest yielding the bluest shades. These methylated and ethylated rosanilines (and para-rosanilines) with a few compounds in which an atom of phenyl, tolyl, or benzyl is introduced, constitute the *aniline violets* of commerce. The following are the most important members of the class :—

Commercial Name.	Chemical Name or Nature.	Formula.
BASIC VIOLETS.		
Methyl violet B. Methyl-aniline violet. Paris violet. (See page 234.)	Hydrochloride of Penta-methyl-pararosaniline.	$\mathrm{C}\left\{\begin{array}{l}C_6H_4.N(CH_3)_2\\C_6H_4.N(CH_3)_2\\C_6H_4.NH(CH_3).Cl\end{array}\right.$
Crystal violet. Violet 6 B. (See page 236.)	Hydrochloride of Hexa-methyl-pararosaniline.	$\mathrm{C}\left\{\begin{array}{l}C_6H_4.N(CH_3)_2\\C_6H_4.N(CH_3)_2\\C_6H_4.N(CH_3)_2.Cl\end{array}\right.$
Benzyl violet. Violet 5 B. Methyl-violet 6 B. extra. Paris violet. (See p. 237.)	Hydrochloride of Penta-methyl-benzyl-pararosaniline (essentially).	$\mathrm{C}\left\{\begin{array}{l}C_6H_4.N(CH_3)_2\\C_6H_4.N(CH_3)_2\\C_6H_4.N(C_7H_7)(CH_3).Cl\end{array}\right.$
Ethyl violet.	Hydrochloride of Hexethyl-pararosaniline.	$\mathrm{C}\left\{\begin{array}{l}C_6H_4.N(C_2H_5)_2\\C_6H_4.N(C_2H_5)_2\\C_6H_4.N(C_2H_5)_2.Cl\end{array}\right.$
Hofmann's violet. Violet 5 R. Dahlia. Primula. (See page 237.)	Hydrochloride (hydriodide or acetate) of Trimethyl- or Triethyl-rosaniline, with admixture of pararosaniline and less substituted compounds.	$\mathrm{C}\left\{\begin{array}{l}C_6H_3(CH_3).NH(C_2H_5)\\C_6H_4.NH(C_2H_5)\\C_6H_4.NH(C_2H_5).Cl\end{array}\right.$ &c.
Regina purple. Phenyl-violet. Imperial violet. (See page 235.)	Acetate of monophenyl- or ortho-tolyl-rosaniline (with admixture of pararosaniline compound).	$\mathrm{C}\left\{\begin{array}{l}C_6H_3(CH_3).NH_2\\C_6H_4.NH(C_7H_7)\\C_6H_4.NH_2.C_2H_3O_2\end{array}\right.$ &c.
Regina violet. Phenyl violet. Spirit violet. (See page 235.)	Hydrochloride (or sulphate) of Diphenyl-rosaniline.	...

Commercial Name.	Chemical Nature or Nature.	Formula.
SULPHONATED VIOLETS.		
Soluble regina violet.	Na salt of Phenyl- or Diphenyl-rosaniline-trisulphonic acid. Trisulphonated spirit-violet. Phenylated acid magenta.	$C\left\{\begin{array}{l}C_6H_2(CH_3)(SO_3Na).NH_2\\C_6H_3(SO_3Na).NH(C_6H_5)\\C_6H_3(SO_3Na).NH(C_6H_5)\\OH\end{array}\right.$
Red violet 4 RS.	Na salt of Dimethylrosaniline trisulphonic acid. Dimethylated acid magenta.	...
Red violet 5 RS.	Na salt of Ethylrosaniline trisulphonic acid. Ethylated acid magenta.	...
Acid violet 6 B (Bayer)	Na salt of Pentamethylbenzyl-pararosaniline sulphonic acid.	$C\left\{\begin{array}{l}C_6H_4.N(CH_3)_2,\\C_6H_4.N(CH_3)_2,\\C_6H_4.N(C_7H_6SO_3Na)(CH_3)\\OH\end{array}\right.$

The aniline violets are usually greenish powders or crystals with metallic reflection, soluble in water to fine violet solutions which dye silk and wool violet without a mordant. They can be fixed on cotton by tannin and tartar-emetic. The aniline violets are decolorised by boiling with potassium cyanide, a turbid solution being produced. With sulphuric acid they dissolve with yellow or brownish-yellow colour, and present a very close analytical resemblance, as will be seen from the annexed tabulated statement (compiled from the descriptions of Schultz and Julius) of their physical characters and chemical reactions.

METHYL VIOLET, METHYL-ANILINE VIOLET, or PARIS VIOLET (page 233), is the hydrochloride or double zinc salt of pentamethylpararosaniline. It is produced by the direct oxidation of dimethylaniline (from dimethyl-toluidine) by cupric chloride:[1]—

$$3C_6H_5.N(CH_3)_2 + 3O = 3H_2O + C_{19}H_{12}(CH_3)_5N_3.$$

A colouring matter known as *chloranil-violet*, probably identical with methyl-violet, is obtained by the reaction of dimethylaniline and chloranil (tetrachlorquinone).

Methyl-aniline violet occurs in commerce as a hydrochloride, and also as a compound of this salt with zinc chloride. The hydrochloride forms small crystals, the zinc double salt a powder or irregular lumps. Both varieties of the colouring matter

---

[1] Sulphate of copper is treated in solution with a large excess of common salt, and acetic acid and dimethylaniline added. The product is moulded into cakes which are dried at 40° to 50° C. These are treated with a quantity of boiling water insufficient to dissolve all the common salt. The aniline violet, being insoluble in strong brine, remains as a residue. It is dissolved in water, the copper removed by sulphuretted hydrogen, and the colouring matter precipitated by treating the filtrate with common salt. It is again purified by re-solution and crystallisation or salting out, or is converted into the zinc double salt.

Colouring Matter.	Appearance.	Solubility.	Aqueous Solution with		Solid Dye with strong Sulphuric Acid.
			Hydrochloric Acid.	Caustic Soda.	
BASIC VIOLETS.					
Methyl-violet B. (See page 234.)	Lumps or powder, with metallic green reflection.	Readily soluble with violet colour.	At first, green; with excess, deep yellowish-brown.	Brown-yellow coloration and ppte.	Yellow; on dilution, yellowish-green, then green-blue, and finally violet.
Crystal-violet. Violet 6 B. (See page 236.)	Crystals, with bronze or beetle-green reflection.	Soluble with violet colour.	First blue, then green, and finally yellow coloration.	Violet ppte. (according to Weingärtner, yellow ppte.).	Yellow; on dilution, green and blue, changing to violet.
Benzyl-violet Violet 5 or 6 B. (See p. 237.)	Lumps or powder, with bronze reflection.	Easily soluble with violet colour.	Same as methyl-violet.	Same as methyl-violet.	Same as methyl-violet.
Ethyl-violet.	Greenish crystalline powder.	Easily soluble with violet-blue colour.	Reddish-yellow solution.	Grey-violet ppte., melting on heating to a brownish oil.	Brown-yellow; on copious dilution, green.
Hofmann's violet. Red shade, 5 R. (See p. 237.)	Greenish crystalline powder.	Soluble with magenta-red colour. Dyes wool bluish-red.	Yellowish-brown colour.	Brown precipitate.	Yellow-brown; no change on dilution.
Hofmann's violet. (Violet shade.)	Lumps with green reflection.	Soluble with blue-violet colour; dyes wool violet.	Green; with excess, yellow.	Brown-red precipitate.	Brownish-yellow; on dilution, olive-green, changing to green and bluish-violet.
Regina purple.	Green powder.	Easily soluble with reddish-violet colour.	Brown colour; becoming blue on dilution.	Brown precipitate.	Cinnamon-brown; no change on dilution.
Regina violet. } Spirit violet. }	Green grains.	Sparingly soluble.	Green flocculent ppte.	Almost complete decoloration.	Brown; on dilution, flocculent violet ppte.
SULPHONATED VIOLETS.					
Soluble regina violet. (See page 234.)	Lumps or powder with bronze reflection.	Soluble with violet colour; dyes wool reddish-violet.	Violet precipitate.	Becomes lighter, but not colourless.	...
Red-violet 4 RS.	Reddish-violet powder.	Easily soluble, with magenta-red colour; dyes wool bluish-crimson.	No change.	On warming becomes pale reddish-yellow.	Brown-yellow; on dilution, magenta-red solution.
Red-violet 5 RS.	Brownish-violet lumps with metallic lustre.	Easily soluble, with magenta-red colour.	No change.	Pale brownish-yellow solution.	Yellow; on dilution, magenta-red solution.
Acid violet 6 B. (See page 234.)	Dark violet powder.	Soluble, with violet colour.	Green, changing to yellow.	No change; with excess of very strong soda, dark violet ppte.	Brownish-yellow; on dilution, green, becoming blue, and finally violet.

exhibit a green metallic reflection, and are easily soluble in water, alcohol, amyl alcohol, and chloroform.

Dilute solutions of methyl violet are turned pure blue by a very small addition of hydrochloric acid. With more acid they appear green in thin layers, but red and somewhat turbid in thicker strata. Excess of acid turns the solution red or yellowish-brown from the formation of an acid salt. Ammonia produces a lilac and caustic soda a violet-brown precipitate, the solution becoming colourless on boiling.

With chromic acid, methyl-violet gives a dirty violet and with stannous chloride a blue-violet precipitate, becoming lighter on boiling. Hypochlorites decolorise solutions of methyl violet.

Methyl violet is completely precipitated by soluble ferrocyanides and ferricyanides, and hence may be conveniently fixed on cotton mordanted with potassium ferrocyanide, or in the fibres of which zinc ferrocyanide has been previously deposited by double decomposition. In this manner methyl violet may be used for printing calico. It is also fixed by albumin or tannin, and is used for topping goods dyed with iron mordants and alizarin, in order to brighten the fast violet thus produced.

Boiling with water gradually decolorises fibres dyed with methyl violet. Hydrochloric acid removes part of the colour and the fibre becomes greenish-yellow, but the original colour is restored on washing with water. Ammonia decolorises the fibre. Caustic soda turns it reddish-violet and gradually decolorises it. Treated with a hydrochloric acid solution of stannous chloride, the fibre becomes a yellow or greenish-yellow colour.

Methyl violet is liable to much the same adulterations as other aniline dyes. It may be determined volumetrically by precipitation with picric acid (page 145), the formula of the picrate being $C_{24}H_{27}N_3.C_6H_2(NO_2)_3OH$.

Crystal Violet is the hydrochloride of hexamethyl-pararosaniline. It is obtained by the reaction of tetramethyl-diamido-benzophenone chloride or carbon oxychloride on dimethylaniline, the reaction in the latter case being :—

$$[C_6H_5.N(CH_3)_2]_3 + 2COCl_2 = Cl.C[C_6H_4.N(CH_3)_2]_3 + 3HCl + CO_2.$$

Crystal violet forms long hexagonal prisms or pyramids. The crystals have a beetle-green reflection if anhydrous, but a variety containing 8 *aqua* also occurs, the reflection from which is bronze. When heated to 100°, the crystals become brown and suffer slight decomposition. Crystal violet is soluble both in water and alcohol, but crystallises more readily from the former than the latter menstruum. The solutions are deep violet-blue, and dye wool and silk a very blue shade of violet. On cotton, crystal violet is fixed by tannin and tartar-emetic.

According to G. Zetter, crystal violet dissolves in strong sulphuric acid with orange colour, which is unchanged on dilution; but according to other observers the solution in sulphuric acid is yellow, changing on dilution to green, blue, and violet.

On adding platinic chloride to a solution of crystal violet in strong hydrochloric acid, the chloroplatinate is obtained as a brick-red precipitate of the composition, $[C_{19}H_{12}(CH_3)_6N_3Cl]_2(PtCl_4)_3$.

On heating crystal violet in a closed tube to 120° C. with an aqueous solution of ammonium sulphide, a leuco-base is formed of the formula $C_{25}H_{21}N_3$, which melts at 173° after being purified by crystallisation from alcohol.

Crystal violet forms a very insoluble picrate, a fact which may be utilised for its determination and assay (see page 145).

Benzyl Violet (pages 233, 235) is prepared by heating methyl violet with benzyl chloride, $C_6H_5.CH_2Cl$, alcohol, and lime or soda, in an apparatus furnished with a reflux condenser. A series of products are thus formed, becoming bluer the greater the number of benzyl atoms introduced into the molecule. The commercial product is the hydrochloride or zinc double salt. Benzyl violet closely resembles methyl violet, but dyes somewhat bluer shades. Fibres dyed by benzyl violet are turned light blue by caustic soda; but if dyed by methyl violet red-violet. In both cases, the material is decolorised after a time.

Hofmann's Violets are of historical interest, being, with the exception of *mauve* (page 257), the first aniline violets produced, but they have now been nearly superseded by the newer colours, such as methyl violet. They are produced by acting on an alcoholic solution of rosaniline with caustic soda and iodide of methyl or ethyl. The larger the proportion of alkyl iodide employed, the greater is the substitution and the bluer the product. The ethylated rosanilines are redder than the corresponding methyl-derivatives.

Aniline Greens.

The green colouring matters derived from triphenylmethane may be divided into two classes, one of which is represented by *methyl green* and the other by *benzaldehyde green*. The former dyes are derivatives of triamido-triphenylmethane, while the latter are derived from diamido-triphenylmethane. The sulphonated aniline greens which are found in commerce are mostly dyes of the latter series.

The following is a list of the principal greens from aniline having a practical interest:—

Commercial Name.	Chemical Name or Nature.	Formula.
Basic Greens. Class I.		
Methyl green. Paris green. Methylaniline green (page 240).	Compound with zinc chloride of hydrochloride of Chlormethyl-hexamethyl pararosaniline.	$C\left\{\begin{array}{l}C_6H_4.N(CH_3)_2\\C_6H_4.N(CH_3)_2.CH_3Cl\\C_6H_4.N(CH_3)_2.Cl\end{array}\right. +ZnCl_2$
Ethyl green. Methyl green (Bayer).	Compound with zinc chloride of the hydrochloride of bromethyl-hexamethyl pararosaniline.	$C\left\{\begin{array}{l}C_6H_4.N(CH_3)_2\\C_6H_4.N(CH_3)_2.C_2H_5Br\\C_6H_4.N(CH_3)_2.Cl\end{array}\right. +ZnCl_2$
Iodine green. Night green (pages 239, 241).	Compound with zinc chloride of the hydrochloride of Chlormethyl-hexamethyl-rosaniline.	$C\left\{\begin{array}{l}C_6H_3(CH_3).N(CH_3)_2\\C_6H_4.N(CH_3)_2CH_3Cl\\C_6H_4.N(CH_3)_2Cl\end{array}\right. +ZnCl_2$
Spirit-soluble green (pages 239, 241).	Picrate of the base of iodine green.	...
Basic Greens. Class II.		
Malachite green. Benzaldehyde green. Victoria green (pages 239, 241). Solid green.	Oxalate of, or compound with zinc or iron chloride of, the hydrochloride of Tetramethyl-diparaamidotriphenylcarbinol.	$3C\left\{\begin{array}{l}C_6H_5\\C_6H_4.N(CH_3)_2\\C_6H_4.N(CH_3)_2.Cl\end{array}\right. +2ZnCl_2$
Brilliant green. New Victoria green. Ethyl green. Solid green J.	Sulphate (or oxalate) of Tetraethyl-dipara-amidotriphenylcarbinol.	$C\left\{\begin{array}{l}C_6H_5\\C_6H_4.N(C_2H_5)_2\\C_6H_4.N(C_2H_5)_2.SO_4H\end{array}\right.$
Victoria green. New solid green.	Hydrochloride (or zinc chloride compound) of Tetramethyl-diamido-dichlor-triphenylcarbinol.	$C\left\{\begin{array}{l}C_6H_3Cl_2\\C_6H_4.N(CH_3)_2\\C_6H_4.N(CH_3)_2.Cl\end{array}\right.$
Sulphonated Greens.		
Helvetia green. Acid green (pages 239, 242).	Na salt of Tetramethyl-diamido-triphenylcarbinol-sulphonic acid. Sulphonated malachite green.	$C\left\{\begin{array}{l}C_6H_4(SO_3Na)\\C_6H_4.N(CH_3)_2\\C_6H_4.N(CH_3)_2\\OH\end{array}\right.$
Acid green (B.A.S.F.).	Na salt of Dimethyldibenzyl-diamido-triphenylcarbinol-sulphonic acid.	$C\left\{\begin{array}{l}C_6H_4(SO_3Na)\\C_6H_4.N(CH_3)(C_7H_7)\\C_6H_4.N(CH_3)(C_7H_7)\\OH\end{array}\right.$
Guinea green B (page 239).	Na salt of Diethyl-dibenzyl-diamido-triphenyl-carbinol-disulphonic acid.	...
Acid green (Bayer). Light green S or SF (page 239).	Na salt of Diethyl-dibenzyl-diamido-triphenyl-carbinol-trisulphonic acid.	$C\left\{\begin{array}{l}C_6H_4(SO_3Na)\\C_6H_4.N(C_2H_5)(C_7H_6SO_3Na)\\C_6H_4.N(C_2H_5)(C_7H_6SO_3Na)\\OH\end{array}\right.$
Fast green (Bayer) (page 239).	Na salt of Tetramethyl-dibenzyl-pseudo-rosaniline-disulphonic acid.	...

The following table is compiled chiefly from the description given by Schultz and Julius (*Chemische Industrie,* 1888) of the physical characters and chemical reactions of the principal green dyes in the foregoing list:—

Colouring Matter.	Appearance, &c.	Solubility.	Aqueous Solution with		Solid Dye with Strong Sulphuric Acid.
			Hydrochloric Acid.	Caustic Soda.	
BASIC GREENS. I. Methyl green.	Green crystals.	Easily soluble in water with bluish-green colour. When strongly heated, becomes violet. Insoluble in amyl alcohol.	Reddish-yellow, becoming yellow-green on dilution.	Reddish; decolorised on dilution without a precipitate being formed.	Reddish-yellow; on dilution yellowish-green.
Ethyl green	Moss-green crystalline powder.	Easily soluble with greenish-blue colour.	Green becoming yellow.	Decolorised.	Yellow; on dilution yellow, becoming green with much water.
Iodine green.	Hard, dark-green fragments.	Same as methyl green.	Reddish-yellow solution.	Decolorised.	Red-yellow; on dilution yellowish-green.
Spirit soluble green.	Dark green paste.	Insoluble in water; green solution in alcohol.	...	...	Red-yellow; on dilution green ppte.
BASIC GREENS. II. Malachite green. Benzaldehyde green.	Green or yellow prisms or leaflets with metallic reflection.	Dissolves with blue-green colour. Picric acid gives green ppte. Soluble in amyl alcohol.	Red-yellow solution.	Decolorised, with formation of pale green ppte. soluble in ether.	Yellow; on dilution dark yellow, changing to yellowish-green, and on further dilution to green.
Ethyl green. Brilliant green.	Crystals with golden reflection.	Soluble with green colour.	Reddish-yellow solution.	Same as malachite green. With ammonia, little or no ppte.	Yellow; on dilution reddish-yellow, changing slowly to yellowish-green and green.
Victoria green 3 B. New solid green 3 B.	Green crystalline powder with metallic reflection.	Very slightly soluble in cold, more readily in hot water, with green-blue colour. Hot solution gelatinises on cooling.	Yellowish-green, becoming yellow with excess.	Reddish-yellow, with a trifling precipitate.	Yellow; on dilution reddish-yellow, and with more water yellowish-green.
SULPHONATED GREENS. Helvetia green.	Bright green powder.	Easily soluble with blue-green colour.	Red-brown crystalline precipitate.	Remains clear, and is decolorised.	Little soluble, with bright-yellow colour; on dilution yellowish-red, changing with more water to yellow-green and green.
Guinea green B.	Dark green, lustreless powder.	Soluble with green colour. $BaCl_2$ gives green precipitate.	Brownish-yellow solution.	Blackish-green precipitate.	Yellow; on dilution yellow-red, then yellow-green, and finally green.
Light green SF.	Bright green, lustreless powder.	Soluble with green colour. $BaCl_2$, no ppte. Picric acid, no ppte.	Yellowish-brown colour.	Decolorised; with dirty violet turbidity.	Yellow; on dilution changes gradually to green.
Fast green (Bayer).	Dark bluish-green crystalline powder.	Soluble with violet colour.	Green, with excess, yellow.	No change; with a large excess of strong soda, dark violet ppte.	Brownish-yellow; on dilution, first green, then blue, and finally violet.

METHYL-GREEN or METHYLANILINE GREEN is the most important of the basic green dyes of Class I. (page 237). It is prepared by acting on pentamethyl-pararosaniline (the base of methyl violet) by methyl chloride, in amylic alcohol solution, and converting the product into the double zinc salt.

Methylaniline green is the double salt with zinc chloride of the hydrochloride of chlormethyl-hexamethyl-pararosaniline,[1] and has the formula :—$C_{19}H_{12}(CH_3)_6N_3.Cl.CH_3Cl + ZnCl_2 + H_2O$. It occurs in commerce either in small green needles, in large coppery prisms, or as a light green powder. It dissolves readily with bluish-green colour in water and alcohol, but is soluble in amyl alcohol. This last character distinguishes methyl green (and probably the other greens of Class I.) from benzaldehyde green (and its allies). Methylaniline green is insoluble in ether or benzene, and may be precipitated from its alcoholic solution by addition of ether.

Dilute acids colour the solution to greenish-yellow, a tri-acid salt being formed, but on dilution with water the original colour is restored. Hypochlorites destroy the colour of methyl green, and stannous chloride and other reducing agents gradually decolorise it.

On adding a strong solution of caustic soda to one of methyl green a resinous precipitate is produced. This precipitate is the free base, and contains $C_{19}H_{12}(CH_3)_6N_3.OH.CH_3Cl$. It is soluble in pure water, and on treatment with moist oxide of silver yields silver chloride and the non-chlorinated base, $C_{19}H_{12}(CH_3)_6N_3.OH.CH_3.OH$, is produced.

As might be expected from its constitution and mode of formation, methyl green readily splits up into methyl chloride and methyl violet. The decomposition occurs gradually at 100°, and rapidly at 120°–130° C. Hence if filter-paper be moistened with a solution of methyl green, and then strongly dried, it will acquire a violet colour. This reaction, which is equally applicable to fibres dyed with the colouring matter, is characteristic of methyl green and its immediate allies (*e.g.*, ethyl green, iodine green).

The adulterations and impurities of methyl green and other aniline greens are described on page 242.

Methyl green is now rarely used for dyeing wool. When it is, sulphur or zinc sulphide is one of the best mordants. Silk is dyed in a warm bath, to which picric, tartaric, or acetic acid is sometimes added. On cotton, methyl green is fixed by means of tannin.

On the fibre, methyl green may be recognised by the change of colour on heating strongly. Excess of hydrochloric acid turns the fibre yellow, but the original colour is restored by washing. The dye is removed by alcohol or acetic acid, the liquid being coloured bluish-green. Alkalies and reducing agents decolorise the fibre.

---

[1] This base may be conveniently referred to as "verdaniline."

Iodine Green (pages 238, 239) presents the closest resemblance to methyl green, with which it is homologous. As formerly prepared, with methyl iodide, it gave off violet vapours of iodine when heated with strong sulphuric acid, but as at present manufactured, by the treatment of rosaniline with methyl chloride, the dye does not give this reaction.

Perkin's green resembles iodine green, but is precipitated by sodium carbonate in the cold.

Spirit-soluble Green (pages 238, 239) is obtained as an insoluble crystalline picrate by adding picric acid to a solution of iodine-green (or methyl-green ?).[1] It often occurs in commerce as a dark green paste, which is nearly insoluble in water but dissolves in alcohol. The solution yields the sparingly soluble yellow potassium picrate on addition of an alcoholic solution of potassium acetate, but picric acid may be extracted by agitating the dye with dilute sulphuric acid and ether. Spirit green sometimes contains an excess of picric acid. This may be detected by placing successive quantities of silk or wool in the alcoholic solution of the dye, until the colouring matter is nearly all taken up. If free picric acid be present, the fibres last added will be dyed yellow. Free picric acid might probably be removed by drying the paste and treating it with ether or benzene.

Benzaldehyde Green, or Malachite Green (pages 238, 239), is obtained by the reaction of dimethyl-aniline on benzaldehyde, whereby tetramethyl-paradiamido-triphenylmethane is produced, thus:—

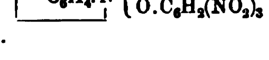
$$C_6H_5.COH + 2C_6H_5N(CH_3)_2 = H_2O + H.C(C_6H_5)[C_6H_4N(CH_3)_2]_2.$$

The hydrochloric acid solution of the product is oxidised by peroxide of lead at 60°–80° C., preferably with addition of a little chloranil. The lead is removed by sodium sulphate, and the filtrate treated with common salt and zinc chloride, when the double zinc compound is precipitated.

The *double zinc chloride* of tetramethyl-diamido-triphenylcarbinol contains $3C_{23}H_{24}N_2,HCl + 2ZnCl_2 + 2H_2O$. It forms brass-yellow prisms, with a yellowish-green reflection.

---

[1] According to Benedikt the picrate contains no chlorine, but P. Julius attributes to it the formula:—



$$C\begin{cases} C_6H_3(CH_3).N(CH_3)_2 \\ C_6H_4.N(CH_3)_2:CH_3Cl \\ C_6H_4.N\begin{cases}(CH_3)_2 \\ O.C_6H_2(NO_2)_3\end{cases} \end{cases}$$

The *double iron chloride* (ferrous) also occurs in commerce as an inferior quality of benzaldehyde green.

The *oxalate*, $C_{23}H_{24}N_2,H_2C_2O_4$, forms scales having a green metallic reflection.

All the commercial forms of benzaldehyde green dissolve easily in water and alcohol. They are also soluble in amylic alcohol, which character distinguishes them from methyl green (and its allies).

The *free base* of benzaldehyde green is obtained as a green precipitate on adding an alkali to the solution of one of its salts. The precipitate is soluble in ether and petroleum spirit, and after crystallisation from the latter solvent forms colourless needles, which melt at 126°–130° C.

The base of malachite green combines with both one and two molecules of picric acid to form insoluble picrates.

The solutions of benzaldehyde green are bluish-green. By concentrated hydrochloric acid they are changed to orange-yellow, but the green colour is restored by dilution. Hypochlorites decolorise the solution, and stannous chloride forms a green precipitate.

Benzaldehyde green may be detected on fibres dyed with it by the orange coloration with hydrochloric acid, restored to green by washing, and by the decolorisation produced by ammonia, soda, or soap. From methyl green it is distinguished by not turning violet when heated.

HELVETIA GREEN is the type of the sulphonated aniline greens, the reactions of which have already been described (page 239). It differs from benzaldehyde green by giving no precipitate with caustic soda in dilute solutions, though strong soda solution produces a white precipitate. On the fibre, acid green closely simulates benzaldehyde green, but is turned greenish-yellow by hydrochloric acid, the liquid itself becoming yellow; whereas fibres dyed with benzaldehyde green become bright orange, and give up very little colour to hydrochloric acid. In each case the original green colour is restored by washing with water. From methyl green, helvetia green is distinguished by the fibres not becoming violet when heated.

ADULTERATIONS OF ANILINE GREENS. Iodine-green varies much in price and quality, the commercial value not always following the dyeing properties, which in samples of the same price may vary as much as 50 per cent. Crystallised greens are usually purer than the amorphous kinds, but not always. Aniline greens vary much in tint, yellow shades being due to picric acid or other yellow dye, and green ones to soluble aniline blue. The latter, when present in small proportion, is best recognised by yellow light. Large amounts may be detected by treating the dye with picric acid and glycerin, when the green remains insoluble, and any blue admixture may be recognised by the colour and characters of the filtered liquid. If the dye be the picrate of "verdaniline" mixed with soluble blue, mere treatment with water is sufficient to detect the admixture. Free picric acid may be detected by agitating with water and ether, and a picrate in the manner already described (page 241).

Some greens contain accidental admixtures of sodium acetate and black insoluble bodies, besides some aniline violet. Methyl green of good quality dissolves entirely in boiling alcohol. If a greenish-white residue be left, which turns violet when heated, it probably consists of the hydrochloride of nonamethylparaleucaniline, $C_{19}H_{13}(CH_3)_6(CH_3Cl)_3$. This body is often present in considerable proportion in methyl-green which has not been purified by alcohol, and is sometimes added as an adulterant.

In water, methyl green should dissolve entirely with bluish-green colour. A residue of green may consist of the picrate, which is entirely soluble in alcohol or dilute caustic soda. The aqueous solution of methyl green should yield no precipitate in the cold with dilute soda or sodium carbonate. A precipitate will probably consist of the base of methyl-violet, which after separation may be recognised by its colour and reactions of its solution in hydrochloric acid. Its presence is due to defective purification of the colouring matter.

Intentional additions of sugar are occasionally made to aniline greens, and compounds of magnesium, lead, and chromium have been met with. Arsenic is found in some samples. Zinc chloride is a normal constituent of soluble and malachite greens.

Comparative tinctorial and dyeing tests are also of value for the examination of aniline greens.

Mixed Greens are made by blending yellow and blue colouring matters. Such products, or the tissues dyed with them, may be examined as follows:—Boil with strong alcohol. Aniline greens are completely dissolved, as also are picrates. Any blue residue will consist of *indigo* or *prussian blue*, which may be distinguished by adding dilute bromine water. The indigo will be bleached, but the prussian blue remains unaffected. On the other hand, prussian blue is turned brown by soda, while indigo remains unchanged. If the alcohol acquire a green colour, aniline blue is present, in which case the original substance or fabric should be boiled with dilute hydrochloric acid, when a blue residue will be left, and the solution can be examined for picric acid and other yellows.

Appendix to the Aniline Dyes.

In the manufacture of magenta and other aniline dyes, certain bye-products are formed, which may be conveniently discussed here, although their constitution is unknown or different from that of the ordinary aniline dyes. The chief products of the kind are *phosphine*, *induline*, and *safranine*. The last of these will be described in a special section (page 256), while *auramine* and *flavaniline*, on the other hand, though not strictly secondary products of the manufacture of magenta, may be conveniently considered in the present connection.

AURAMINE. $C_{17}H_{21}N_3,HCl+H_2O$. By the action of carbon oxychloride on dimethylaniline in presence of aluminium chloride, tetramethyl-diamido-benzophenone is produced, and when this body is heated with ammonium chloride and zinc chloride to 150°–160° C., it reacts to form an imido-tetramethyl-diamido-diphenylmethane. The reactions are represented by the following formulæ:—

$$COCl_2+2C_6H_5.N(CH_3)_2=2HCl+CO\left\{\begin{array}{l}C_6H_4.N(CH_3)_2\\C_6H_4.N(CH_3)_2\end{array}\right.;\ \text{and}$$

$$CO\left\{\begin{array}{l}C_6H_4.N(CH_3)_2\\C_6H_4.N(CH_3)_2\end{array}\right.+NH_3=C\left\{\begin{array}{l}C_6H_4.N(CH_3)_2\\C_6H_4.N(CH_3)_2\\:NH\end{array}\right.$$

The new body is a colourless base, which forms salts of an intensely yellow colour, the hydrochloride being the *auramine* of commerce. The hydrochloride, sulphate, and acetate are readily soluble in water, but the thiocyanate and double zinc salt are only very sparingly soluble in cold water.

Commercial auramine is a sulphur-yellow powder, which dissolves somewhat sparingly in cold, but more readily in hot water, to form a bright yellow solution. It is also soluble in alcohol. The cold aqueous solution is unchanged by hydrochloric acid, but on boiling the liquid is decolorised, with re-formation of ammonium chloride and tetramethyl-diamido-benzophenone. On addition of caustic soda, the aqueous solution of auramine yields a white precipitate of the free base. The precipitate dissolves on agitation with ether, and the separated ethereal solution is not fluorescent, but communicates a yellow colour to acetic acid when shaken with it. When treated with zinc and acetic acid, auramine gives an evanescent green coloration. Alkaline reducing agents, such as sodium amalgam or zinc and ammonia, gradually decolorise the alcoholic solution of auramine, and on adding water a colourless reduction-product is precipitated, which when heated with acetic acid yields a deep blue colour.

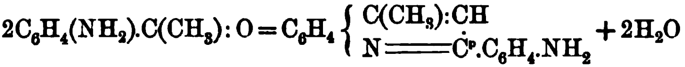
Auramine produces a brilliant and very pure yellow when mordanted on cotton with alizarin oil or tannin and a salt of antimony.[1] The fibre is decolorised both by acids and alkalies.

If in the manufacture of auramine the ammonium chloride be replaced by the hydrochlorides of aniline, xylidine, naphthylamine, &c., substituted auramines are obtained, none of which appear to crystallise, and which dye shades ranging from yellow to light brown.

FLAVANILINE. $C_{16}H_{14}N_2,HCl$. When acetanilide is heated with zinc chloride to a temperature of 250°–270° C., it is converted into a colouring matter, the free base of which has the constitution of a para-amidophenyl-γ-lepidine, or γ-lepidine-aniline. The reaction consists in the conversion of acetanilide into the isomeric ortho-amido-acetophenone, the subsequent conversion of a portion of this into *para*-amido-acetophenone, and the coalescence of one molecule of each of these bodies with elimination of water, thus:—

$$C_6H_5.NH.C(CH_3):O \quad = C_6H_4(NH_2).C(CH_3):O$$

Acetanilide. *Amido-acetophenone.*



$$2C_6H_4(NH_2).C(CH_3):O = C_6H_4 \left\{ \begin{array}{l} C(CH_3):CH \\ N{=\!=\!=}\dot{C}^{p}.C_6H_4.NH_2 \end{array} \right. + 2H_2O$$

Amido-acetophenone. *Para-amidophenyl-lepidine.*

Flavaniline is now almost obsolete in commerce. It is a hydrochloride of the base, and occurs as an orange-yellow crystalline powder, readily soluble in water with yellow colour. The solution is unchanged by hydrochloric acid, but on adding soda yields a milky precipitate of the free base, soluble in ether, without colour, but with steel-blue fluorescence. In strong sulphuric acid, flavaniline dissolves with dirty-yellow colour and blue fluorescence. Flavaniline dyes wool and silk yellow without a mordant. Silk dyed with flavaniline exhibits a fine moss-green fluorescence.

Flavaniline S is a sulphonated flavaniline. It resembles the basic dye, but the solution is gradually decolorised by soda without a precipitate being formed. In strong sulphuric acid it forms a colourless solution, becoming yellow on dilution.

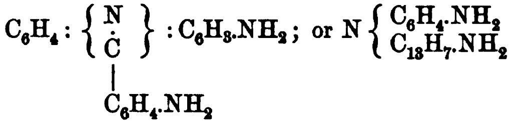
CHRYSANILINE. PHOSPHINE. This colouring matter, also called

---

[1] Auramine is one of the few artificial yellow dyes which can be fixed on the fibre by means of tannin. Hence it may be employed to produce very yellow shades of malachite green on cotton.

aniline yellow, *aniline orange*, and *leather yellow*, is obtained as a secondary product of the manufacture of magenta.[1]

Pure chrysaniline has the constitution of a diamido-phenyl-acridine:[2]—



$$\begin{array}{l} C_6H_4 : \left\{ \begin{matrix} N \\ \dot{C} \end{matrix} \right\} : C_6H_3.NH_2 ; \text{ or } N \left\{ \begin{matrix} C_6H_4.NH_2 \\ C_{13}H_7.NH_2 \end{matrix} \right. \\ \qquad\quad | \\ \qquad C_6H_4.NH_2 \end{array}$$

The commercial product *phosphine* is usually the nitrate or according to Benedikt the hydrochloride, of chrysaniline, mixed with more or less of the corresponding salt of the homologue chrysotoluidine, $C_{20}H_{17}N_3$.

Commercial *phosphine* forms an orange-yellow powder, readily soluble if the hydrochloride, but difficultly if the nitrate, to a reddish-yellow solution. It is also soluble in alcohol. Dilute hydrochloric acid simply deepens the colour, but with excess of the strong acid a dihydrochloride is precipitated, readily soluble in pure water. Ammonia and soda liberate free chrysaniline as an amorphous yellow precipitate, which melts on boiling, the liquid being coloured pale yellow. The precipitate is soluble in ether. Phosphine dissolves in strong sulphuric acid to form a reddish-yellow solution which exhibits a strong green fluorescence. On dilution, a reddish-yellow solution is obtained.

On adding nitric acid or sodium nitrate to a tolerably concentrated solution of phosphine, the sparingly soluble chrysaniline nitrate separates as a red crystalline precipitate. In warm solutions, the precipitate is produced slowly, and on stirring the liquid is deposited in streaks in the track of the glass rod. Under the microscope the precipitate is seen to consist of needles. This characteristic reaction, when carefully applied, distinguishes phosphine from other yellow colouring matters, but is liable to fail in solutions of the nitrate. Hence a preferable plan is to liberate the base by ammonia, agitate with ether, treat the separated ethereal solution with dilute acetic acid, concentrate the acetic solution, and add sodium nitrate. This mode of operating excludes the possibility of confusion with nitro-compounds, which often yield yellow crystalline precipitates on treating their solutions with nitric acid or potassium nitrate. But the nitro-dyes are not extracted by agitating their ammoniacal solutions with ether, though, unlike chrysaniline, most of them are extracted from their acidulated solutions. Nitro-compounds are further distinguished by the red or brownish colour developed on boiling with potassium cyanide; whereas phosphine gives a yellow precipitate in the cold, and the liquid acquires a yellow colour on boiling.

---

[1] The resinous bye-products contain chrysaniline, mauvaniline, violaniline, a little rosaniline, and undefined resinous matters. On boiling the mass with dilute hydrochloric acid, resins and violaniline remain insoluble. By fractional precipitation of the filtered solution with lime, mauvaniline, rosaniline, and chrysaniline are successively precipitated. Chrysaniline may be more easily prepared from the mother-liquors which remain after precipitating the magenta by salt, in the arsenic acid process. More salt is added to the liquid and then lime, the precipitate treated with dilute nitric acid, and the sparingly soluble nitrate of chrysaniline precipitated by adding excess of nitric acid to the solution. The deliberate synthesis of chrysaniline has been effected by heating benzoic acid and diphenylamine with zinc chloride, nitrofying the resultant phenylacridine, and reducing it to the diamido-derivative.

[2] For further information on the constitution of chrysaniline and flavaniline, see an interesting lecture by R. Meldola, *Jour. Soc. Dyers, &c.*, ii. 95, from *Jour. Soc. Arts*, May 28, 1886. Benzoflavine is a diamido-dimethyl-phenylacridine (*Jour. Soc. Dyers, &c.*, v. 2).

On treatment with stannous chloride and hydrochloric acid, chrysaniline solutions are decolorised, but the yellow colour rapidly returns on exposing the reduced liquid to the air.

When heated with 3 or 4 parts of hydrochloric acid to 160°–180° C., chrysaniline is decomposed with formation of ammonium chloride and chrysophenol, $C_{19}H_{15}N_2O$, in the same way that flavaniline yields flavenol, and auramine tetramethyl-benzophenone.

Phosphine behaves to fibres like the other basic aniline dyes. It produces a yellow on silk or wool, and is used in admixture with magenta for dyeing silk scarlet. On cotton mordanted with aluminium acetate it gives a nankin-yellow which will stand soaping.

Acids redden fibres dyed with phosphine, and after a time the colouring matter is removed. Alkalies turn the fibre to a greenish-yellow paler than the original. Reducing agents decolorise it gradually.

Mauvaniline, $C_{19}H_{17}N_3,H_2O$, is a base of unknown constitution contained in magenta-residues. It must not be confounded with mauveine or Perkin's purple, which is related to the safranines (page 257). It is prepared by boiling the resinous residue from the arsenic acid process with dilute hydrochloric acid, and precipitating the bases from the filtered solution by excess of lime. The washed precipitate is sold as *maroon paste*, or is neutralised by hydrochloric acid, and thus rendered soluble in water. If the soluble maroon so obtained be fractionally precipitated with common salt, the hydrochloride of mauvaniline is thrown down first, while the rosaniline and chrysaniline salts remain in solution. The product may be purified by crystallisation from boiling water.

The hydrochloride of mauvaniline is crystalline, and exhibits a fine bronze reflection. It dissolves sparingly in cold water, more readily in hot, to a blue-violet solution, from which alkalies precipitate the free base. It dyes silk and wool a fine and fast violet.

Mauveine, the base of *mauve*, is another product of the oxidation of aniline containing toluidine. It is probably related to the safranines, with which colouring matters it will be described (page 257).

Indulines and Nigrosines.

The name induline is applied to a series of basic bodies formed by the reaction of amido-azo-compounds on the hydrochlorides of aromatic amines (*e.g.*, aniline), with elimination of ammonia. The substances of the induline class occurring in commerce are dark-blue or violet dyes, less remarkable for their brilliancy than their resistance to light and atmospheric influences.

Violaniline, $C_{18}H_{15}N_3$, the typical member of the class, is a base contained in the commercial colouring matters known as *nigrosine* and *induline*. It is a product of the oxidation of aniline ($C_6H_7N + O_3 = C_{18}H_{15}N_3 + 3H_2O$), and may be prepared by heating aniline with nitrobenzene and iron filings to 180° C. Violaniline is often present in magenta-residues, from which it may be prepared by boiling with hydrochloric acid, which dissolves the other bases, and leaves violaniline hydrochloride and resinous matters undissolved. On treating these with boiling aniline, and filtering, the pure colouring matter separates out on cooling. The hydrochloride so obtained is a bluish-black amorphous powder, insoluble in water but soluble in alcohol with bluish-violet colour. The free base is precipitated in flakes on adding an alkali to this solution.

Violaniline may also be prepared by heating together aniline and amido-azobenzene (page 178) in molecular proportions, when the new colouring matter is produced with evolution of ammonia: —$C_6H_7N + C_{12}H_{11}N_3 = C_{18}H_{15}N_3 + NH_3$. The dye obtained by heating hydrochloride of aniline with amido-azobenzene to 160° in alcoholic solution, is called *azo-diphenyl blue*, and is probably identical with *induline B*. It is distinguished from induline 3 B (see below) by its readier solubility in alcohol, its redder shade of colour, and the brownish-red colour of the free base.

By heating violaniline with aniline, or by using excess of aniline in its manufacture, phenylated substitution-products are obtained, the highest of which is triphenyl-violaniline, $C_{18}H_{12}(C_6H_5)_3N_3$.

By increasing the proportion of aniline hydrochloride, a series of indulines are obtained, the identity of which is determined by the proportions of the reagents and the temperature employed.

If two parts of diazo-amidobenzene (page 177), one of aniline hydrochloride, and four of aniline be mixed and allowed to stand for twenty-four hours, to allow of the conversion of the diazo-amido-azobenzene into the metameric body amido-azobenzene, and the mixture be then heated to 125°–130°, a more complex reaction ensues,[1] and a base is produced, the hydrochloride of which crystallises from the liquid on cooling. The free base has the formula $C_{30}H_{23}N_5$, and forms warty crystals, soluble in alcohol with dark purple colour. The hydrochloride is the *induline 3 B* of commerce, and forms brownish shining scales, soluble with purple colour in aniline or alcohol, and is used for producing delicate fast greys on cotton, for which fibre it has some little affinity.

By increasing the proportion of aniline hydrochloride in the melt, and raising the temperature to 165°–170° C., a base is obtained of the formula $C_{30}H_{22}(C_6H_5)N_5$, which crystallises from aniline in needles having a green metallic reflection. The hydrochloride, $C_{36}H_{27}N_5,HCl$, is the *induline 6 B* of commerce, and forms green lustrous crystals which readily lose hydrochloric acid.

Blue dyes of the induline class are obtained when amido-azonaphthalene is substituted by amido-azobenzene; but if the aniline be replaced by orthotoluidine or amido-naphthalene, red colouring matters are produced.

The characters and reactions of the various commercial indulines are not strictly identical, but do not require separate description. As a class, the indulines usually occur as bluish-black or brownish-black powders, which are insoluble in water but soluble in alcohol with greenish or bluish-violet colour. The alcoholic solution becomes pure blue with hydrochloric acid, and on adding soda yields a dirty-red or reddish-violet solution or precipitate, the exact reaction depending on the nature of dye under examination. In strong sulphuric acid, the indulines dissolve with blue colour, a violet-blue precipitate being formed on dilution. Treatment with zinc and ammonia decolorises the solutions on warming, but the original colour returns on exposure to air. The benzene solution exhibits an intense red-brown fluorescence.

SULPHONATED INDULINES. SOLUBLE INDULINES. By treating the indulines with strong sulphuric acid, various sulphonated indulines are obtained which are soluble in water. The redder shades are met with in commerce under the name of *fast blue R* and *water-soluble nigrosine*, and the bluer varieties as *fast blue B*, *fast blue*

---

[1] If the temperature be limited to 100°, the product consists largely of azophenine, $C_{36}H_{29}N_5$, a base which crystallises from hot aniline in small, garnet-red plates, melting at 236°, and forming a violet solution in strong sulphuric acid which becomes azure-blue at 300°, and exhibits a carmine-red fluorescence on dilution with water.

greenish, *induline 3 B* or *6 B*, &c. These sulphonated indulines occur as crystalline powders with a bronze reflection ("induline"), or as black, glistening fragments ("nigrosine"). They dissolve in water with bluish-violet, and in alcohol with blue colour. Hydrochloric acid renders the solution blue. Alkalies produce a brownish-violet precipitate. In sulphuric acid, the sulphonated indulines dissolve with blue colour, changing to violet on dilution with water. By oxidation they yield quinone and other products, and by reducing agents are converted into unstable leuco-derivatives.

Soluble indulines are used for the preparation of coloured inks, and both the soluble and insoluble in the preparation of spirit-varnishes. They are very fast dyes, and are employed for producing grey, bluish, and blue-black shades on wool, silk, leather, &c., and are used as indigo-substitutes. In commerce they are met with under a variety of names, including, besides those already mentioned, *Blackley blue*, *Guernsey blue*, *indigo-substitute*, *bengaline*, *Coupier's blue*, &c.

On the fibre, the indulines are turned somewhat bluer by hydrochloric acid, but nitric acid is almost without action (distinction from indigo). Ammonia and soda strip the fibre, forming reddish-violet solutions, which are decolorised by zinc powder, but the colour returns on filtering and exposing the liquid to the air. An acid solution of stannous chloride strips the fibre, and forms a green solution. Hypochlorites bleach some indulines, and turn others reddish-grey.

ANILINE BLACK. By the oxidation of aniline under suitable conditions a very stable black colouring-matter is formed. The most perfect black is yielded by pure aniline boiling at 182° C. Orthotoluidine gives a bluish-black and paratoluidine a brown-black.[1]

The oxidation of aniline to aniline black may be effected by potassium bichromate, permanganate, or chlorate, and by various other oxidising agents. In practice, a readily changeable metallic salt is employed as a carrier of oxygen, a very suitable combination being a chlorate (preferably that of sodium) and cupric sulphate. Ammonium vanadate now receives a large application in the production of aniline black, as it is readily reduced to vanadium chloride, and this is immediately reoxidised to a vanadate by the chlorate simultaneously employed. One part of vanadium will do the duty of 4000 of copper, and suffice for the production of from 10,000 to 20,000 parts of aniline black. Electrolytic oxygen may also be employed for producing aniline black.

---

[1] NAPHTHAMEÏN, or Naphthalene Violet, is a colouring matter produced by treating the hydrochloride of alphanaphthylamine with ferric chloride or other oxidising agent. It forms an amorphous, purple precipitate, insoluble in water, alkalies, and dilute acids, and only sparingly soluble in alcohol, but readily soluble in ether or acetic acid. In strong sulphuric acid it dissolves with blue colour.

To produce aniline black in a pure state, 40 parts of aniline hydrochloride, 40 of cupric sulphate, 20 of potassium chlorate, and 16 parts of ammonium chloride should be dissolved in 500 parts of water, and the solution heated to about 60° C. The black precipitate formed may be purified, if desired, by boiling it successively with hydrochloric acid, alcohol, ether, benzene, and chloroform. The product is the hydrochloride of a base called nigraniline, which may be obtained in a free state by treating the colouring matter with a dilute alkali.

Nigraniline has the empirical formula C_6H_5N, and consequently possesses the same centesimal composition as azobenzene (page 175). Its molecular formula, according to Nietzki, is probably $C_{30}H_{25}N_5$. According to Liechti and Suida, however, aniline black is a chlorinated base called emeraldine, containing $C_{18}H_{14}ClN_3$, all the salts of which contain chlorine, which cannot be removed even by treatment with argentic oxide. Nigraniline is a weak base, and combines with two equivalents of acids to form a series of dark green salts, which are insoluble in and partially decomposed by water.

Aniline black is turned dark green by sulphurous acid, and other mineral acids also affect it; but if it be treated with an acid solution of potassium bichromate the black colour becomes permanent, and is no longer affected by treatment with acids or reducing agents. According to Liechti and Suida, this unalterable black is not a chromate of the base, but the compound of an oxidation-product with chromic oxide (Cr_2O_3).

By treatment with tin and hydrochloric acid, aniline black is reduced to paradiamidobenzene, paradiamidodiphenylamine, and other products.

Powerful oxidising agents, such as chromic acid mixture, convert aniline black into quinone, $C_6H_4O_2$.

Aniline black dissolves in strong sulphuric acid to form sulphonic acids, which are insoluble in acidulated water, and are therefore precipitated on adding water to the solution. On protracted washing with water the precipitate dissolves with green colour. The alkali-metal compounds of sulphonated aniline black dissolve in water with blue-black colour. The solutions are decolorised by reducing agents (*e.g.*, zinc-powder, glucose), but recover their original tint on exposure to air. The fact is employed for the preparation of an aniline-black vat.

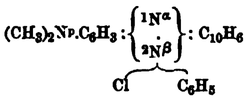
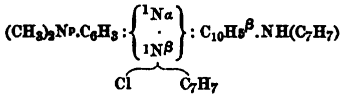
On heating aniline-black with aniline acetate, an induline is formed (page 248), the hydrochloride of which crystallises in needles having a cupreous lustre.

Aniline-black differs remarkably from most other aniline colours in that it is wholly insoluble in water, alcohol, acids, soap-lye, and alkaline solutions. Hence the application of ready-formed aniline-black is very limited, and it is usually produced in the fibre itself. It yields an extremely fast and pure black on cotton, but it is not well suited for dyeing silk or wool.

On the fibre, aniline-black is easily recognised by its resistance to reagents,[1] being unchanged by alkalies, and either wholly unchanged by acids or turned slightly greenish, the black colour being restored by alkalies. Weak oxidising agents have no effect, but if the fibre be treated alternately with strong solutions of potassium permanganate and oxalic acid, several times in succession, the colour will be destroyed. Hypochlorites change the colour to brownish-red, but if the fibre thus treated be washed and exposed to the air it slowly becomes black again.

SAFRANINES AND THEIR ALLIES.

The colouring matters of this class are, or can be, obtained by the reaction of nitrosodimethylaniline or its analogues on various aromatic amines and phenols. The dyes thus produced may be arranged under the four heads of safranines, eurhodines, indophenols, and oxazines. The following table shows the names and formulæ of the more important colouring matters of these classes. Mauveine (page 257) is probably related to the safranines, but its constitution has not been ascertained with certainty.

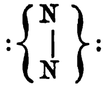
Commercial Name.	Chemical Name or Nature.	Formula.
I. SAFRANINES.		
Neutral Blue.	Chloride of phenyl-dimethyl-paramido-pheno-naphthazonium.	 $(CH_3)_2N^p.C_6H_3:\underbrace{\left\{\begin{matrix}{}^1N^{\alpha}\\ \cdot\\ {}^2N^{\beta}\end{matrix}\right\}}_{Cl\qquad C_6H_5}:C_{10}H_6$
Basle Blue.	Chloride of tolyl-dimethylamidopheno-tolylimido-naphthazonium.	 $(CH_3)_2N^p.C_6H_3:\underbrace{\left\{\begin{matrix}{}^1N\alpha\\ \cdot\\ {}^1N\beta\end{matrix}\right\}}_{Cl\qquad C_7H_7}:C_{10}H_5{}^{\beta}.NH(C_7H_7)$

---

[1] Fibres dyed with *logwood black* leave on ignition an ash containing iron or chromium, as also do *madder* and *tannin blacks*. These blacks are reddened by dilute hydrochloric acid, and are readily bleached by bromine water or hypochlorites.

Commercial Name.	Chemical Name or Nature.	Formula.
Phenosafranine. Safranine B extra. (See page 254.)	Chloride of paramidophenyl-paramidophenazonium.	$H_2N^p.C_6H_3 : \underbrace{\left\{\begin{matrix}{}^2N^2\\ .\\ {}^1N^1\end{matrix}\right\}}_{Cl \qquad {}^1C_6H_4{}^p.NH_2} : C_6H_4$
Safranine (page 256) Safranine T. Safranine extra G.	Mixture of Tolusafranine and phenotolusafranine.	$H_2N^p.C_6H_2(CH_3)_3 : \underbrace{\left\{\begin{matrix}{}^2N^2\\ .\\ {}^1N^1\end{matrix}\right\}}_{Cl \qquad C_6H_4.{}^pNH_2} : C_6H_3(CH_3)^p$
Giroflé. Amethyst.	Chloride of xylyl-dimethyl-amidophenyl-xylylazonium.	$(CH_3)_2N^5.C_6H_3 : \underbrace{\left\{\begin{matrix}{}^2N^2\\ .\\ {}^1N^1\end{matrix}\right\}}_{Cl \qquad {}^1C_6H_2 - \left\{\begin{matrix}{}^2CH_3\\ {}^pNH_2\\ {}^5CH_3\end{matrix}\right.} : C_6H_2(CH_3)^p(CH_3)^6$
Magdala Red. Naphthalene Red. Soudan Red. Rosanaphthylamine (page 257).	Chloride of diamidonaphthyl-naphthazonium.	$H_2N.C_{10}H_5 : \underbrace{\left\{\begin{matrix}N\\ .\\ N\end{matrix}\right\}}_{Cl \qquad C_{10}H_6.NH_2} : C_{10}H_6$
II. EURHODINES.		
Neutral Violet. (See page 258.)	Hydrochloride of Dimethyl-diamidophenazine.	$(CH_3)_2N^p.C_6H_3 : \left\{\begin{matrix}{}^1N^1\\ .\\ {}^2N^2\end{matrix}\right\} : C_6H_3{}^p.NH_2.HCl$
Neutral Red. (See page 258.)	Hydrochloride of Dimethyl-diamidotoluphenazine.	$(CH_3)_2N^p.C_6H_3 : \left\{\begin{matrix}{}^1N^1\\ .\\ {}^2N^2\end{matrix}\right\} : C_6H_2(CH_3).NH_2.HCl$
III. INDOPHENOLS.		
Indophenol. Naphthol Blue (page 258).	Oxidation-product of Dimethylparamidophenylalphaoxy-naphthylamine.	$\left.\begin{matrix}(CH_3)_2N.C_6H_4.N\\ \vert\\ O\end{matrix}\right\} : C_{10}H_6$
White Indophenol. Reduced Indophenol (page 259).	(Tin compound of) Dimethylparamidophenyl-alphaoxy-naphthylamine.	$\left.\begin{matrix}H\\ (CH_3)_2N.C_6H_4.\dot{N}\\ O\\ \dot{H}\end{matrix}\right\} : C_{10}H_6$
Phenol Blue.	Dimethyl-paramidophenyl-oxyphenylamine.	$\left.\begin{matrix}(CH_3)_2N.C_6H_4.N\\ .\\ O\end{matrix}\right\} : C_6H_4$
IV. OXAZINES.		
Gallocyanin. Solid Violet (page 259).	Chloride of Dimethylphenyl ammonium-dihydroxy-phenoxazine-carbonic acid.	$Cl.(CH_3)_2N.C_6H_3 : \left\{\begin{matrix}{}^1N^1\\ {}^2O^2\end{matrix}\right\} : C_6H \left\{\begin{matrix}{}^3OH\\ {}^4OH\\ {}^6CO.OH\end{matrix}\right.$
Prune (page 259).	Methyl ether of Gallocyanin.	$Cl.(CH_3)_2N.C_6H_3 : \left\{\begin{matrix}{}^1N^1\\ {}^2O^2\end{matrix}\right\} : C_6H \left\{\begin{matrix}OH\\ OH\\ CO.O(CH_3)\end{matrix}\right.$
Naphthalene Blue. Meldola's Blue. New Blue (page 260).	Chloride of Dimethyl-phenylammonium-betanaphoxazine.	$Cl.(CH_3)_2N.C_6H_3 : \left\{\begin{matrix}{}^1N\\ {}^2O\beta\end{matrix}\right\} : C_{10}H_6$
Muscarin (page 260).	Chloride of Dimethyl-phenyl-parammonium betaoxynaphthoxazine.	$Cl.(CH_3)_2N.C_6H_3 : \left\{\begin{matrix}{}^1N^\alpha\\ {}^2O^\beta\end{matrix}\right\} : C_{10}H_5.OH^\beta$
Nile Blue (page 260).	Chloride or sulphate of Dimethyl-phenyl-parammonium-alpha-amidonaphthoxazine.	$Cl.(CH_3)_2N.C_6H_3 : \left\{\begin{matrix}{}^1N\alpha\\ {}^2O\beta\end{matrix}\right\} : C_{10}H_5.NH_2{}^\alpha$

Safranines. The dyes of this class all contain the group:—



$$:\left\{\begin{matrix}N\\|\\N\end{matrix}\right\}:$$

The two unsatisfied bonds are usually united to phenylene either substituted or intact, but in a few cases are satisfied by $C_{10}H_6$. In addition, one or both of the nitrogen atoms exercise pentavalent functions, as will be seen on reference to the foregoing table. This constitutes a distinction between the safranines and the eurhodines, as in the latter both the nitrogen atoms appear to be trivalent (see page 253).

A general method for the production of the safranines consists in the oxidation of one molecule of a paradiamido-base with two molecules of a mono-amido-base in a hot, neutral, aqueous solution.[1] Potassium bichromate is a suitable oxidising agent. The simplest member of the class, namely, phenosafranine, is obtained by oxidising a mixture of paradiamido-benzene and aniline hydrochloride, $C_6H_8N_2 + 2C_6H_7N + 2O_2 = C_{18}H_{14}N_4 + 4H_2O$.

The safranines of commerce are the chlorides of compound ammonium bases called azoniums. The free bases are but little known. Their salts, which usually crystallise well, are red or violet dyes, the dilute aqueous solutions of which give no precipitate with alkalies. On treatment with dioxidising agents they are reduced to colourless leucosafranines, which readily absorb oxygen from the air, with re-formation of the original colouring matters.

The safranines mostly dissolve in strong sulphuric acid with fine green colour. On gradually adding water, the colour of the liquid changes first to bluish-green, and then to a pure blue. With still more water, the solution becomes violet-blue, and ultimately acquires the colour of an aqueous solution of the dye under examintion. The green solution absorbs the violet, blue, and red rays of the spectrum, and the bluish-green behaves similarly, but absorbs the red less perfectly; the blue solution absorbs only yellow light; and as by dilution the colour changes to violet and red, the region of absorption approaches the green.

The following Table exhibits the chief properties and reactions of the safranines of commercial importance. Their constitutional formulæ are given on pages 252 and 253.

---

[1] Safranines are also formed when one molecule of meta- or para-toluidine, or of methyl- or dimethyl-aniline, is substituted for one of aniline. Both molecules of aniline may be similarly substituted by metatoluidine, but with two molecules of paratoluidine or of methyl- or dimethyl-aniline the formation of the colouring matter does not take place.

Name.	Formula.	Appearance, &c.	Solubility in Water.	Alcoholic Solution.	Reaction of Aqueous Solution with		With Strong Sulphuric Acid.
					Hydrochloric Acid.	Caustic Soda.	
Neutral Blue.	$C_{24}H_{20}N_3Cl$	Brown lustreless powder.	Easily soluble, with violet colour.	Violet-red colour.	No change; with large excess colour becomes bluer.	Violet percipitate.	Brownish-violet; on dilution, violet solution.
Basle Blue.	$C_{32}H_{29}N_4Cl$	Brown crystalline powder.	Bluish-violet solution; decolorised by warming with zinc dust.	...	Blue precipitate.	...	Greenish-brown solution; on dilution, green changing to violet liquid, and finally bluish-violet precipitate.
Phenosafranine. Safranine B. extra.	$C_{18}H_{15}N_4Cl$	Green glittering crystals.	Easily soluble with red colour. The solution is decolorised by warming with zinc dust, and again becomes red in the air.	...	With little acid the solution becomes somewhat blue; with excess, violet; and concentrated acid turns a strong solution blue.	Reddish-brown precipitate, soluble in much water.	Green solution; changing on dilution to blue, violet, and red.
Safranine. Safranine extra G. (see p. 256).	$C_{21}H_{21}N_4Cl$	Reddish-brown powder.	Soluble with red colour.	Red, with yellowish-red fluorescence.	Blue-violet coloration.	Brownish-red precipitate.	Green solution; on dilution, blue changing to red.
Giroflé., Amethyst.	$C_{24}H_{27}N_4Cl$	Brown paste or greyish-green powder.	Soluble with magenta-red colour.	Red.	In dilute solution, no change; concentrated, blue.	Red precipitate, soluble in much water.	Green solution, becoming blue and red on dilution.
Magdala Red. Naphthalene Red. Rosanaphthylamine. Soudan Red (page 257).	$C_{30}H_{21}N_4Cl$	Dark-brown crystalline powder.	Difficultly soluble on heating.	Cherry-red, with cinnabar-red fluorescence.	Colour becomes somewhat more violet.	Reddish-violet coloration; fluorescence destroyed.	Greyish-violet solution; on dilution, violet-red precipitate.
Mauveine. Rosolan. Mauve. Perkin's purple (page 257).	$C_{27}H_{25}N_4Cl$	Reddish-violet paste.	Insoluble in cold; on heating, difficultly soluble with violet-red colour.	...	No change.	Bluish-violet precipitate insoluble in ether.	Olive-green solution; on dilution, first green then blue, and finally reddish-violet.

The only colouring matters of the safranine group requiring further description are the following :—

Safranine, Safranine T, Safranine extra G, or Aniline Pink. This colouring matter, as it occurs in commerce, is a mixture of several homologous bodies, of which $C_{19}H_{17}N_4Cl$, $C_{20}H_{19}N_4Cl$, and $C_{21}H_{21}N_4Cl$ are the chief. The structural formula of the second of these is shown on page 253. Safranine can be obtained by various methods, including the oxidation of mauveine, $C_{27}H_{25}N_4Cl$; the treatment of aniline with glacial acetic acid and lead nitrate; and by heating amido-azotoluene with toluidine nitrate. These methods are obsolete, that now employed being usually the oxidation of a mixture of aniline, ortho-toluidine and para-toluylene-diamine in molecular porportions. Aniline oil of suitable composition is first converted into the amido-azo-compounds amido-azobenzene and amido-azotoluene (page 178). When reduced with zinc and hydrochloric acid, the first of these splits into aniline and paraphenylene-diamine, and the latter into ortho-toluidine and paratoluylene-diamine (page 213); thus—

$$C_6H_4(CH_3).N_2.C_6H_3(CH_3).NH_2 + 2H_2 = C_6H_4(CH_3).NH_2 + NH_2.C_6H_3(CH_3).NH_2 .$$

When the reaction is complete the liquid is diluted, a molecular proportion of toluidine hydrochloride added, and the mixture oxidised by potassium bichromate. The product is boiled with milk of lime, and the liquid filtered, neutralised with hydrochloric acid, and saturated with salt. The precipitate is purified by solution in water, and again salting out.

Commercial safranine usually occurs as a reddish-brown powder, but the pure hydrochloride forms reddish crystals, soluble in water and alcohol. The alcoholic solution exhibits a fine yellowish-red fluorescence. Caustic alkalies and ammonia change the colour of an aqueous solution of safranine to brownish-red, but no precipitate is produced unless the liquid is concentrated. The base is best prepared by treating a solution of the hydrochloride with argentic oxide, filtering, and evaporating the filtrate to dryness.

Safranine is one of the few colouring matters which are taken up by animal fibres from alkaline solutions. In alkaline or neutral solution safranine also possesses some affinity for cotton, but the colour produced is not fast. The best mordant is tannin and tartar-emetic.

On the fibre, safranine is distinguished by being unchanged by dilute acid but turned from red to blue-violet by concentrated hydrochloric acid. Ammonia and caustic soda remove the colouring matter without much previous change of tint. The colour is bleached on warming the fibre with hydrochloric acid and stannous chloride. Alcohol strips fibres dyed with safranine, forming a red solution which exhibits a reddish-yellow fluorescence.

MAGDALA RED. NAPHTHALENE RED. $C_{30}H_{21}N_4Cl + H_2O$ (see pages 253, 255). This colouring matter is prepared by heating α-naphthylamine in acetic acid solution to 150° with a molecular proportion of alpha-amido-azonaphthalene (prepared by diazotising alpha-naphthylamine hydrochloride). The melt is boiled with a large excess of hydrochloric acid, and the liquid filtered. The filtrate is neutralised, and salt gradually added, when the rosanaphthylamine is precipitated as a sparingly soluble hydrochloride, and a violet colouring matter and excess of naphthylamine remain in solution.

Naphthalene red is characterised by its very sparing solubility in water, even when hot, and by forming a cherry-red alcoholic solution, which exhibits a fluorescence of a remarkable cinnabar-red colour. This behaviour is simulated only by an alkaline solution of azoresorufin (page 158); but that substance differs from naphthalene red in the colour it dyes silk, and in yielding a brown precipitate on addition of a strong acid. The fluorescence of a solution of naphthalene red is destroyed by ammonia or soda.

Magdala red is employed for producing a fluorescent pink on silk and velvet. It is not used on wool. Neither the shade nor fluorescence is altered in artificial light. It is distinguished from *eosin* by not being stripped from the fibre by alcohol, and by not being readily affected by alkalies or dilute acids.

MAUVEINE, $C_{27}H_{24}N_4$, is of interest as being the base of *Perkin's purple*, *aniline violet*, or *mauve*, the first commercial dye from aniline. The free base may be obtained by adding caustic alkali to a boiling alcoholic solution of the crystallised acetate. It then separates as a black glistening powder, which is almost insoluble in ether or benzene, but in alcohol forms a violet solution, which is turned purple on adding a dilute acid, or even by carbonic acid. Mauveine is a strong base, decomposing ammonium salts and forming a carbonate.

Commercial mauve is usually a sulphate of the base. It is now almost obsolete, but occasionally occurs as a reddish-violet paste, sparingly soluble in hot water with violet-red colour. The solution is unchanged by hydrochloric acid, but yields a bluish-violet precipitate with soda, and dyes silk a reddish-violet. In an excess of strong sulphuric acid, mauve dissolves with olive-green colour, changing on adding water to green, sky-blue, and finally to a reddish-violet.

Eurhodines.

O. N. Witt defines the eurhodines as dye-stuffs which are derived from azines by the replacement of an atom of hydrogen by an amido-group, thus differing from the safranines, which contain two amido-groups, and are the salts of azonium-bases (page 254). Neutral violet and neutral or toluylene-red, the formulæ of which have been already given (page 253), are the only dyes of the eurhodine class requiring detailed description.

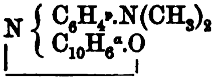
Neutral Violet, $C_{14}H_{14}N_4,HCl$ (page 253), is produced by the reaction of nitroso-dimethylaniline on meta-phenylenediamine. The commercial colouring matter is a greenish-black powder, the dust of which is intensely irritating to the mucous membrane. It dissolves easily in water with violet-red colour. The solution is scarcely changed by a little hydrochloric acid, but is turned blue by excess. Soda produces a brown precipitate. In concentrated sulphuric acid the dye dissolves with green (or, according to Zetter, dirty violet) colour, which on adding water becomes blue, and on further dilution violet.

Neutral Red or Toluylene Red, $C_{15}H_{16}N_4,HCl$ (page 253), is homologous with the last colour. It forms a greenish-black powder easily soluble in water with bluish-red colour, which turns bluer and then disappears on warming with zinc and hydrochloric acid, but returns on exposing the reduced solution to the air. In alcohol the dye dissolves to a magenta-red solution, which exhibits a strong brownish-red fluorescence. With hydrochloric acid the aqueous solution becomes bluer, and with excess pure blue. With soda it yields a yellowish-brown precipitate, soluble in ether with greenish-yellow fluorescence. In strong sulphuric acid, toluylene red dissolves with bluish-green colour, changing to blue and magenta-red on adding water.

Indophenols.

When a phenol is substituted for an aromatic monamine in the process for the preparation of safranines (pages 254, 256), colouring matters are produced which are called indophenols. The chief member of the class is prepared by reducing nitrosodimethylaniline in aqueous solution to dimethyl-paraphenylenediamine, $NH_2.C_6H_4.N(CH_3)_2$, filtering, and treating the filtrate with a solution of two molecules of alpha-naphthol in caustic soda. Potassium bichromate is next added, and then acetic acid till the liquid acquires an acid reaction, when the colouring matter is precipitated. Indophenol may also be obtained by the direct action of nitro-dimethylaniline on alpha-naphthol.

Indophenol or Naphthol Blue, $C_{18}H_{16}N_2O$, prepared as above, is a feeble base which probably has the constitution expressed by the formula :—



$$N\left\{\begin{array}{l}C_6H_4^{p}.N(CH_3)_2\\ C_{10}H_6^{\alpha}.O\end{array}\right.$$

This is borne out by its reduction by stannous acetate to a leuco-body possessing both acid and basic properties, and having the formula:—

$$N\left\{\begin{array}{l}C_6H_4.N(CH_3)_2\\ C_{10}H_6.OH\\ H\end{array}\right.$$

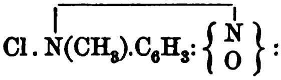
Commercial *indophenol N* forms a blue paste or dark brown powder, which when dry has a coppery reflection and closely resembles some varieties of indigo. When heated it sublimes in needles. Indophenol is quite insoluble in water, but dissolves in alcohol with blue colour, and in strong sulphuric acid with dirty yellowish-brown colour, the solution giving a brown precipitate on dilution. The alcoholic solution is turned reddish-brown by hydrochloric acid, but is unchanged by alkalies. The alkaline solution, or the solid dye in presence of alkali, is decolorised by reducing agents, such as stannous chloride or glucose, so that a vat can be prepared from indophenol in the same way as from indigo.

Reduced Indophenol, or **White Indophenol**, $C_{18}H_{18}N_2O$, occurs in commerce as a yellowish-white paste, soluble in pure or acidulated water. It is unchanged by hydrochloric acid. In presence of an alkali and air it gradually oxidises to blue indophenol, or immediately on cautious treatment with bichromate of potassium or a hypochlorite.

Indophenol is employed as a substitute for indigo in wool and cotton dyeing. It forms a lake with chromic oxide. On the fibre it is best recognised by being turned greyish-brown or dark grey by treatment with somewhat dilute (10 per cent.) hydrochloric acid, while indigo and other dark blue dyes are unaffected.

Oxazines.

(See also page 253.) These colouring matters are produced by the action of phenoloïds on a *salt* of nitroso-dimethylaniline or an allied body. All the oxazines contain the group:—



$$Cl.N(CH_3).C_6H_3:\left\{\begin{array}{c}N\\ O\end{array}\right\}:$$

, or $ClC_6H_9N_2O$:

Gallocyanin, or Solid Violet, $C_{15}H_{13}N_2O_5Cl$ (page 253), occurs usually in commerce as a nearly insoluble, greenish-grey paste, which forms a bronze powder on drying. The characters of pure gallocyanin are described on page 74.

Prune, $C_{16}H_{15}N_2O_5Cl$ (page 253), is the methyl ether of gallocyanin, and forms small bronze crystals or a dark brown powder. It is soluble in water and alcohol with bluish-violet colour. Hydrochloric acid turns the solution magenta-red, and soda gives first a brown precipitate, and with excess of the reagent a violet solution. In concentrated sulphuric acid the dye dissolves with corn-flower blue colour, changing to magenta-red on dilution.

MELDOLA'S BLUE, or NEW BLUE (Casella), $C_{18}H_{15}N_2OCl$ (page 253), called also *fast blue 2 B for cotton* and *naphthalene blue R in crystals,* is produced by the reaction of betanaphthol on nitrosodimethylaniline hydrochloride. It occurs in commerce as a dark violet powder with bronze reflection. The dust strongly irritates the mucous membrane. In water it is soluble with bluish-violet colour; in alcohol with blue colour. The violet aqueous solution becomes at first green and then colourless when reduced by zinc and acetic acid, the original colour returning on exposure to air. The solution is turned blue by hydrochloric acid, and with soda yields a brown precipitate. In strong sulphuric acid the dye dissolves with blackish-green colour, becoming first blue and then violet on dilution. Naphthalene blue dyes cotton mordanted with tannin and tartar-emetic an indigo-blue colour.

MUSCARIN, $C_{18}H_{15}N_2O_2Cl$, introduced by Durand and Haguenin, occurs in commerce as a brown-violet powder, sparingly soluble in cold but readily in hot water, with bluish-violet colour. The solution is decolorised by heating with zinc-dust, but the colour returns on exposure to air. Hydrochloric acid produces a bluish-violet and soda a yellowish-brown precipitate. Tannin precipitates the solution indigo-blue. In concentrated sulphuric acid muscarin dissolves with bluish-green colour,[1] the solution turning first blue and then violet on adding water, and on further dilution giving a violet precipitate.

NILE BLUE is produced by the reaction of alpha-naphthylamine on the hydrochloride of nitroso-dimethyl-metamidophenol. It occurs in commerce both as the *chloride,* the formula of which has already been given (page 253), and as a *sulphate* of the composition $(C_{18}H_{16}N_3O)_2SO_4$. The *sulphate* forms a green crystalline powder with bronze reflection. It is sparingly soluble in cold water, but readily on warming, with blue colour. It is also soluble in alcohol. The warm concentrated aqueous solution yields with hydrochloric acid needles of the chloride, which appear violet by transmitted and green by reflected light. Addition of soda to the dilute solution (1:1000) produces a red precipitate, soluble in ether to a brown-orange solution, with dark green fluorescence. Tannin in presence of sodium acetate gives a prussian-blue precipitate, and stannous chloride a dark greenish-blue precipitate, and on warming the liquid exhibits a green fluorescence, with blue transmitted light. In concentrated sulphuric acid, the dye dissolves with yellow or red-brown colour, changing to green and blue on dilution. Wool is dyed directly by nile blue a red shade of blue, and cotton mordanted with tannin and tartar-emetic is dyed blue. The colour is not fast to light, and is liable to bleed when milled with soap, but not with soda.

---

[1] According to some authorities, reddish-violet.

COLOURING MATTERS FROM ANTHRACENE.

The coloured derivatives of anthracene are limited in number, and even of these few have any practical value as dyes. They differ materially from the coal-tar dyes hitherto considered, though presenting considerable resemblance between themselves, and several members of the group are colouring matters of the first importance.[1]

The starting point in the production of alizarin and allied colouring matters is commercial anthracene, containing from 50 to 55 per cent. of the pure hydrocarbon, $C_{14}H_{10}$, or sometimes a purer product, obtained by sublimation, is employed. This is suspended in water and treated with 1½ times its weight of potassium bichromate and an equivalent quantity of sulphuric acid, when the anthracene is converted into anthraquinone, $C_{14}H_8O_2$. The product is separated by filtration, dried, treated with strong sulphuric acid (sp. gr. 1·84), and the mixture heated to 105°–110° C. The black product is treated with steam, which is absorbed by the sulphuric acid, and as the dilution proceeds the anthraquinone crystallises out. Boiling water is then added, and the product well washed with hot water and solution of soda to remove associated organic acids, after which it is further purified by sublimation or distillation in a current of superheated steam. The product contains from 96 to 98 per cent. of real anthraquinone, and forms golden-yellow prismatic needles, melting at 273° C., insoluble in water, highly stable and indifferent, and unacted on by bases or dilute acids (see vol. ii. page 515).

Anthraquinone has a constitution expressed by the formula $C_6H_4\colon\left\{\begin{matrix}CO\\CO\end{matrix}\right\}\colon C_6H_4$. When treated with fuming sulphuric acid containing 50 per cent. of the anhydride, it yields anthraquinone-monosulphonic acid, the sodium salt of which if fused for several days at 180° to 200° C. with caustic soda, and sufficient potassium chlorate or nitrate to prevent reduction by the hydrogen evolved, yields sodium alizarate,[1] thus:—

---

[1] The money value of artificial alizarin and the allied colours is more than one-third of that of the total coal-tar dyes, and the price of alizarin, compared tinctorially, is not more than one-fourth of what it was in the form of madder and garancine.

$$C_6H_4{:}C_2O_2{:}C_6H_3SO_3Na + 3H(ONa) = C_6H_4 : C\,O_2{:}C_6H_2(ONa)_2 + Na_2SO_3 + H_2O + H_2.$$

On dissolving the melt in water and adding hydrochloric acid, free *alizarin*, or ortho-dihydroxy-anthraquinone, $C_6H_4 : C_2O_2 : C_6H_2(OH)_2$, is precipitated.

If, in the treatment of the anthraquinone with fuming sulphuric acid, an excess of the reagent be employed, instead of the monosulphonic acid a *beta*-disulphonic acid is the chief product; but if the temperature be increased to 180°–185°, the isomeric *alpha*-disulphonic acid is the more abundant.[2]

On fusing the alpha-disulphonic acid of anthraquinone with caustic soda, it is converted into the sodium salt of anthraflavic acid, while the beta-acid when thus treated yields the isomeric body iso-anthraflavic acid. Both these substances are dihydroxyanthraquinones, like alizarin, and dissolve in alkalies with yellow colour, but have no dyeing properties. If the fusion of the alpha- and beta-disulphonic acids of anthraquinone with caustic soda be conducted in presence of an oxidising agent, the products are the sodium salts of flavopurpurin and anthrapurpurin respectively. Both these bodies are valuable dye-matters, and have the constitution of trihydroxy-anthraquinones, $C_6H_4 : C_2O_2 : C_6H(OH)_3$, the difference between them being due to the positions of the hydroxyl groups. They are both isomeric with the natural substance purpurin, contained in madder, which has been obtained synthetically by oxidising alizarin in solution in concentrated sulphuric acid (page 270). Anthragallol is a fourth trihydroxy-anthraquinone, obtained by the action of phthalic anhydride on pyrogallol in sulphuric acid solution. (See page 270.)

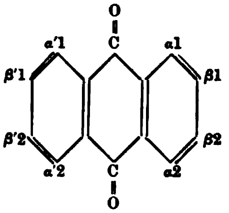
Several tetrahydroxyanthraquinones (*e.g.*, anthrachrysone, hydroxypurpurin, rufiopin) are known, while rufigallic acid (see page 67) has the constitution of a hexahydroxy-anthraquinone.

---

[1] If the fusion be conducted in the absence of air, and no oxidising agent be added, the sodium compound of mono-hydroxyanthraquinone is formed.

[2] On converting the mixed product into sodium salts and adding dilute sulphuric acid, the sparingly soluble monosulphonate can be separated from the easily soluble acid sodium salts of the two isomeric disulphonic acids.

The constitution of anthraquinone derivatives is best interpreted by the aid of the "benzene-chain."



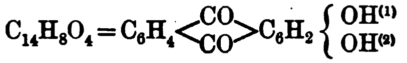
The diagram represents the constitution of anthraquinone, an atom of carbon being situated at each angle, and combined at the *a* and *β* positions with an atom of hydrogen. By the replacement of one or more of these hydrogen atoms by a corresponding number of hydroxyl groups, various hydroxy-derivatives of anthraquinone are obtainable, and their constitution, so far as it is known, will be understood by comparing the following table with the diagram:—

Name.	Formula.	Position of Substituted H atoms.	Melting Point °C.
ANTHRAQUINONE,	$C_{14}H_8O_2 = C_6H_4 : C_2O_2 : C_6H_4$	..	278
MONOHYDROXYANTHRAQUINONES,	$C_{14}H_7O_2(OH)$		
Erythrohydroxyanthraquinone,	$C_6H_4 : C_2O_2 : C_6H_3(OH)$	α1	..
Beta-hydroxyanthraquinone,	Do.	β1	323
DIHYDROXYANTHRAQUINONES,	$C_4H_6O_2(OH)_2$.		
Alizarin,	$C_6H_4 : C_2O_2 : C_6H_2(OH)_2$	α1 ; β1	289-290
Purpuroxanthin,	Do.	α1 ; β2	262-263
Quinizarin,	Do.	α1 ; α2	194
Chrysazin,	$C_6H_3(OH) : C_2O_2 : C_6H_3(OH)$	α'1 ; α1	191
Anthrarufin,	Do.	α'2 ; α1	..
Anthraflavic acid,	Do.	β 2 ; β1	Above 330
Isoanthraflavic acid,	Do.	β1' ; β1	Above 330
Anthraflavone,	Do.	?	291-293
Frangulic acid,	Do.	?	252-254
Isoalizarin,	Do.	?	..
TRIHYDROXYANTHRAQUINONES,	$C_{14}H_5O_2(OH)_3$		
Anthragallol,	$C_6H_4 : C_2O_2 : C_6H(OH)_3$	α1 ; β1 ; β2	..
Purpurin,	Do.	α1 ; β1 ; α2	..
Anthrapurpurin,	$C_6H_3(OH) : C_2O_2 : C_6H_2(OH)_2$	β'1 ; α1 ; β1	About 360
Flavopurpurin,	Do.	β'2 ; α1 ; β1	Above 330
Hydroxychrysazin,	Do.	?	..
TETRAHYDROXYANTHRAQUINONES,	$C_{14}H_4(OH)_4O_2$		
Anthrachrysone,	$C_6H_2(OH)_2 : C_2O_2 : C_6H_2(OH)_2$	?	320
Hydroxypurpurin,	..	?	
Rufiopin,	..	?	
HEXHYDROXYANTHRAQUINONES,	$C_{14}H_2(OH)_6O_2$		
Rufigallic acid (page 67),	$C_6H(OH)_3 : C_2O_2 : C_6H(OH)_3$	?	

By the oxidation of methyl-anthracene, $C_{14}H_9(CH_3)$, a series of products parallel to the above may be obtained. Chrysophanic acid, $C_6H_4:C_2O_2:C(CH_3)(OH)_2$ (see page 281), is a dihydroxy-methylanthraquinone, while emodin is a trihydroxy-derivative.

Such of the hydroxy-derivatives of anthraquinone as receive practical application are not known generally by their systematic or descriptive names, but are simply termed "alizarin for reds," "alizarin for blues," &c. Hence it will be convenient to describe fully the characters of true alizarin, and subsequently treat of the various products known in commerce as "alizarin."

Alizarin. Ortho-dihydroxy-anthraquinone.



$$C_{14}H_8O_4 = C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}C_6H_2\left\{\begin{matrix}OH^{(1)}\\OH^{(2)}\end{matrix}\right.$$

Alizarin exists ready-formed in madder-root (*Rubia tinctorum*), but the proportion of actual alizarin is, except in old roots, small compared with that existing potentially in the form of ruberythric acid,[1] a glucoside which on steeping the madder roots in water is resolved, under the influence of a peculiar ferment called erythrozyme, into alizarin and dextro-glucose, according to the following equation:—

$$C_{26}H_{28}O_{14} + 2H_2O = C_{14}H_8O_4 + 2C_6H_{12}O_6.$$

Various methods of accelerating this change have been devised, the most important and rational being to treat the powdered root, previously exhausted with water, with strong sulphuric acid, which splits up the ruberythric acid according to the foregoing equation, without altering the resultant alizarin. The product thus obtained was called garancine, but the cultivation of madder as a source of alizarin is now almost entirely abandoned, and garancine and similar products have little more than an historical interest.

Alizarin is now manufactured artificially on a very large scale, the sole source being the anthracene from coal-tar. The synthesis of alizarin was first effected by Graebe and Liebermann, in 1868. One of the methods employed in practice has already been described in outline (page 261). The other commercial process, devised by W. H. Perkin, consists in converting anthracene into dichloranthracene, $C_{14}H_8Cl_2$, by the action of chlorine, and heating the product with sulphuric acid, whereby a mixture is obtained of the two isomeric anthraquinonedisulphonic acids described on page 262, with more or less of the monosulphonic acid. The subsequent fusion with an alkali and an oxidising agent, and decomposition of the sodium salts by an acid is the same as that already described. To obtain pure alizarin, a pure monosulphonic acid (free from the disulphonic acid) must be employed,[1] and hence Perkin's process is better adapted for the production of anthrapurpurin and flavopurpurin than true alizarin.

---

[1] RUBERYTHRIC or RUBIANIC ACID, $C_{28}H_{24}O_{14}$, may be obtained by exhausting fresh madder-root with water, adding neutral lead acetate, filtering, and decomposing the precipitate of lead rubianate by sulphuretted hydrogen. On evaporating the liquid filtered from the lead sulphide, rubianic acid is obtained in yellow silky needles.

Alizarin may also be prepared by heating phthalic anhydride with catechol, a reaction which indicates its constitution:—

$$C_6H_4:(CO.OH)_2+C_6H_4:(OH)_2=C_6H_4:(CO)_2:C_6H_2(OH)_2+2OH_2.$$

Alizarin crystallises from alcohol in reddish-yellow prisms or needles containing 3 *aqua*, which it loses at 100°. It melts at 289°–290° C.,[2] and sublimes at a somewhat higher temperature in magnificent orange-red needles.

Alizarin is nearly insoluble in cold water, and requires 3220 parts of boiling water for solution. Cold alcohol dissolves it but sparingly, but in boiling alcohol, glacial acetic acid, and glycerin it is more soluble. It is also readily soluble in ether, carbon disulphide, and benzene, and may be extracted by agitation with these solvents. In strong sulphuric acid, alizarin dissolves with dark brownish-red colour, and is precipitated unchanged on diluting the solution with water.

In solutions of alum and aluminium sulphate alizarin is almost insoluble, a character which distinguishes it from purpurin, which dissolves in boiling alum solution, forming a yellowish-red and strongly fluorescent liquid (page 270).

Alizarin has the characters of a weak acid. It dissolves in solutions of carbonates of the alkali-metals, apparently without decomposing them, and it also dissolves in a boiling solution of sodium acetate, separating again unchanged on cooling; but if the boiling be continued for some time, acetic acid is given off and sodium alizarate remains in permanent solution. With caustic alkalies it reacts to form true compounds or *alizarates*, the solutions of which are violet by transmitted, and purple by reflected, light. A solution of sodium alizarate gives insoluble, coloured precipitates or "lakes" with most metallic solutions. Thus with barium and calcium salts it yields purple precipitates (distinction from monohydroxyanthraquinone) which are soluble in water containing carbonic acid. With aluminium and tin alizarin forms red lakes, and has such affinity for these metals that it is capable of decomposing dilute solutions of nitrates or chlorides containing them. With ferric salts, sodium alizarate yields a black-violet precipitate, but with ferrous salts a violet precipitate is formed. An alcoholic solution of free alizarin also gives a purple precipitate with ferric chloride.

---

[1] To obtain pure alizarin, the blue shade of commercial alizarin paste may be dissolved in dilute caustic soda, and the filtered solution treated with barium chloride and heated to boiling. Barium alizarate separates as a precipitate, which is filtered off, washed, and decomposed by hydrochloric acid. The free alizarin is well washed, and can be further purified by sublimation or crystallisation from glacial acetic acid.

[2] This is the melting point of alizarin according to Claus and Wildgerodt. Schunck gives 282° as the melting point.

By heating in the solid state with zinc-dust, alizarin is reduced to anthracene, $C_{14}H_{10}$. If dissolved in weak soda and treated in the cold with zinc-dust, the violet solution becomes red. When alizarin is boiled with zinc-dust and ammonia it is reduced to a body of the formula $C_{14}H_{10}O_3$, to which the name anthrarobin has been given.[1]

The solution of alizarin in ammonia or carbonated alkali differs from that of purpurin in being non-fluorescent, but exhibits a characteristic absorption-spectrum, having a well-defined band in the yellow, and another narrower one between the orange and red. There is also another faint band about E, scarcely distinguishable from the general absorption occurring in that region. The absorption spectra of the solutions of alizarin in ether and carbon disulphide are not characteristic (compare page 272).

When boiled with acetic anhydride, alizarin yields a monoacetyl-derivative, and on prolonged boiling diacetylalizarin, $C_{14}H_6(O.C_2H_3O)_2O_2$.

ALIZARIN-SULPHONIC ACID. $C_{14}H_5O_2(OH)_2(SO_3H)$. This body is formed by heating alizarin with fuming sulphuric acid until the product is completely soluble in water. The liquid is then diluted, and the unaltered sulphuric acid precipitated by lime or baryta.

---

[1] ANTHRAROBIN has been recommended in skin-diseases as a substitute for chrysarobin or chrysophanic acid (page 283), as it is said to be less liable to produce inflammation of the cuticle. It is prepared by boiling commercial alizarin with zinc-dust and dilute ammonia, filtering the ammoniacal solution into hydrochloric acid, and collecting, washing, and drying the precipitate. The similar product from purpurin is called *anthrarobin P* or *T*.

Commercial anthrarobin is a yellowish-white powder, permanent in the air, and insoluble in water and dilute acids, but readily soluble with brownish-yellow colour in dilute solutions of alkalies and alkaline earths, the solutions by contact with air or oxygen changing to green and blue, and finally to violet.

Anthrarobin dissolves with difficulty in benzene or chloroform, but is soluble with moderate facility in cold, and very easily in boiling alcohol. The alcoholic solution may be mixed with glycerin without precipitation.

Commercial anthrarobin contains a trace of zinc, but the entire ash should not exceed 0·3 per cent.

Alizarin-sulphonic acid is freely soluble in water, and forms three series of salts, according to the number of hydrogen atoms replaced. The salts of the alkali-metals containing one atom of base are yellow or orange, and soluble in water; those with two atoms are reddish-violet; and those with three atoms intensely violet.

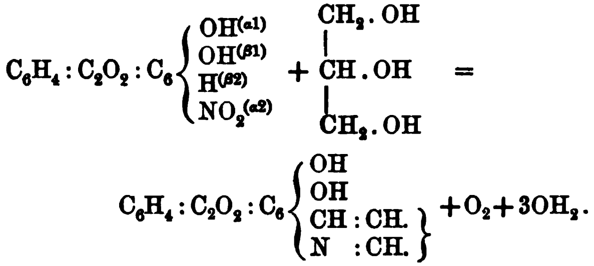
Sodium Alizarin-sulphonate, $C_{14}H_5O_2(OH)_2(SO_3Na)$, constitutes the colouring matter known in commerce as *alizarin carmine*, *alizarin powder W*, and *alizarin WS* or *WSI*. It forms an orange-yellow powder, easily soluble in water or alcohol with orange or brownish-yellow colour. The solution is turned bright yellow by hydrochloric acid and violet by caustic soda. In strong sulphuric acid the dye dissolves with yellowish-red colour, changing to bright yellow on dilution. Alizarin carmine dyes wool mordanted with alumina scarlet, while tin mordants give orange and chromium claret-red shades; but the colours are not so bright as those obtained with sulphonated azo-dyes.

BETA-NITROALIZARIN. $C_6H_4:C_2O_2:C_6H(NO_2)(OH)_2$. By direct treatment with nitric acid, alizarin is converted into phthalic acid, $C_6H_4(COOH)_2$ (page 47); but by the action of nitric acid on alizarin dissolved in glacial acetic acid or petroleum spirit, beta-nitro-alizarin is obtained. This body, which constitutes the *alizarin orange* of commerce, was formerly prepared by exposing cloth dyed with alizarin red to nitrous fumes, but is now directly obtained by treating alizarin in nitrobenzene solution with nitric acid of 30°–40° Baumé. When pure, nitro-alizarin forms yellow needles or leaflets, which melt at 244° C. and sublime at a higher temperature with partial decomposition. It is nearly insoluble in water, but dissolves in glacial acetic acid. The solution in caustic soda is magenta-red, and on treatment with zinc-dust gradually becomes blue and then yellowish-brown, the indigo-blue colour returning on exposing the filtered liquid to the air. Other reactions of alizarin orange are given on page 276.

β-nitro-alizarin derives its chief practical interest from its reaction with glycerol and sulphuric acid,[1] whereby it is converted in dihydroxyanthraquinone-quinoline, or *alizarin blue*, according to the following equation:—

---

[1] One part of nitro-alizarin in fine powder is heated with five parts of strong sulphuric acid and five of absolute glycerin to 150° C. When the reaction is completed, the product is boiled with excess of water, when the colouring matter dissolves, but is deposited on cooling as a flocculent brown precipitate. When this is washed with water, it loses sulphuric acid and becomes blue.



$$C_6H_4:C_2O_2:C_6\left\{\begin{matrix}OH^{(\alpha 1)}\\OH^{(\beta 1)}\\H^{(\beta 2)}\\NO_2^{(\alpha 2)}\end{matrix}\right. + \begin{matrix}CH_2.OH\\|\\CH.OH\\|\\CH_2.OH\end{matrix} = C_6H_4:C_2O_2:C_6\left\{\begin{matrix}OH\\OH\\\left.\begin{matrix}CH:CH.\\N\ \ :CH.\end{matrix}\right\}\end{matrix}\right. + O_2 + 3OH_2.$$

Alizarin Blue, $C_{17}H_9NO_4$, has the constitutional formula shown above. In the pure state it forms dark blue or brownish-violet needles, which melt at 270°, and may be partially sublimed without decomposition. In commerce, alizarin blue occurs as minute shining crystals, or as a dark violet paste containing 10 per cent. of the dry substance. The pure colouring matter can be obtained by boiling the dried paste with glacial acetic acid, the alizarin blue being deposited in crystals on cooling. It is insoluble in water, but dissolves with blue colour in hot alcohol, and is sparingly soluble in benzene.

Alizarin blue exhibits both acid and basic characters, a property doubtless due to the simultaneous presence of OH groups and a pyridine residue in the molecule. With dilute sulphuric acid alizarin blue unites to form a brown compound, which is decomposed by washing with water. In strong sulphuric acid it dissolves with red, and in phosphoric and arsenic acids with reddish-yellow colour.

In dilute caustic alkalies alizarin blue dissolves with greenish-blue colour, but the solution is precipitated by excess of alkali. By treating the solution of alizarin blue in caustic alkali with metallic solutions a series of insoluble lakes may be obtained. The compounds with lime, baryta, and ferric oxide are greenish-blue, that with nickel oxide blue, and those with alumina and oxide of chromium bluish-violet.

When treated with zinc-dust in alkaline solution, alizarin blue is reduced with red coloration, but the blue colour returns on exposing the filtered liquid to the air. Other reducing agents may be employed, and the property may be applied for the production of an alizarin blue vat, similar to that used in indigo-dyeing. Alizarin blue is too expensive to be used generally as a substitute for indigo, and its tendency to form insoluble lakes is not in its favour. The colour is not so fast to light as indigo, but is less readily attacked by oxidising agents, such as hypochlorites, chromic acid, and alkaline solutions of ferricyanides.

The inconvenience attending the employment of ordinary alizarin blue can be overcome by converting it into a soluble form, by treating the commercial paste with a concentrated solution of acid sodium sulphite. After standing ten days or a fortnight, the liquid is filtered, and the new colouring matter obtained in the solid state by evaporation at a low temperature or salting out.

ALIZARIN BLUE S, or *Soluble Alizarin Blue*, obtained as above described, is the sodium bisulphite compound of dihydroxyanthraquinone-quinoline. It occurs in commerce as a dark purple or chocolate-brown powder, which dissolves easily in water with yellowish-brown colour. In strong sulphuric acid the solid dye dissolves with deep yellow colour, and on dilution with water the liquid yields a brownish precipitate. Dilute hydrochloric acid changes the colour of the aqueous solution to reddish-yellow, and soda turns it bluish-violet. With excess of a strong acid or alkali, the bisulphite compound is decomposed with precipitation of the blue; but the solution is unaffected by salts of calcium, magnesium, or chromium, or by acetic or tartaric acid. On heating the aqueous solution above 70° C., the bisulphite compound is decomposed, and the insoluble blue colouring matter is precipitated. This reaction is extensively applied in practice, and the colour produced being less affected by light than that given by insoluble alizarin blue, the soluble variety has almost superseded the older colouring matter both in printing and dyeing.

Soluble alizarin blue is now a formidable rival of indigo in wool-dyeing. The wool is first mordanted by sulphuric acid and bichromate of potassium, and is then immersed in a bath of alizarin blue S, to which sufficient acetic acid has been added to neutralise any earthy carbonates existing in the water. The colours thus obtained are said to be as fast as indigo to light and milling.[1]

On the fibre, alizarin blue is unchanged by soap, soda, or solution of bleaching powder. When dyed on wool with a chrome mordant, nitric acid produces an orange colour, but otherwise the colour is discharged. Dilute hydrochloric solution turns the colour to violet, and soda to bluish-green, while an acid solution of stannous chloride changes the colour to a brownish-yellow. When treated with phosphoric acid of 1·435 sp. gravity, alizarin blue is dissolved from the fibre with orange colour, and the solution, after dilution with water, is turned blue on adding ammonia. The absorption-spectrum of alizarin blue is characteristic, and the fact may be utilised for its detection.

---

[1] Alizarin blue is now being tried on a large scale in the Prussian army, the English navy, and on the Atlantic liners.

Trihydroxyanthraquinones. $C_{14}H_5O_2(OH)_3$.

Of the five known bodies of this constitution (formulated on page 263) four have a practical interest as colouring matters, and are described below. Of hydroxychrysazin, the fifth discovered isomer, very little is known.

Anthragallol. $C_6H_4{:}C_2O_2{:}C_6H(OH)_3.[OH{:}OH{:}OH = \alpha 1{:}\beta 1{:}\beta 2]$. This body has not yet been obtained from anthracene. It is prepared by the action of phthalic anhydride on pyrogallol in presence of sulphuric acid or chloride of zinc:—

$$C_6H_4 : C_2O_2 : O + C_6H_3(OH)_3 = C_6H_4 : C_2O_2 : C_6H(OH)_3 + H_2O\,.$$

It may also be obtained by acting with gallic acid on benzoic acid in presence of sulphuric acid:—

$$C_6H_5.CO.OH + C_6H_2(OH)_3.CO.OH = C_6H_4{:}C_2O_2{:}C_6H(OH)_3 + 2H_2O\,.$$

Anthragallol forms the essential constituent of the colouring matter known as *anthracene brown.* It occurs as a dark brown paste, insoluble in water, but dissolving in alcohol with yellow colour. Its other reactions are described on page 276.

Purpurin. $C_6H_4{:}C_2O_2{:}C_6H\,(OH)_3\,[OH{:}OH{:}OH = \alpha 1{:}\beta 1{:}\alpha 2]$. Purpurin occurs to a considerable amount in old madder-root, mixed with alizarin, from which it may be separated by treating the mixture with a boiling solution of alum, in which alizarin is insoluble. Purpurin may also be prepared artificially by oxidising alizarin or quinizarin (page 263) with manganese dioxide and sulphuric acid. A preferable plan is to dissolve alizarin in strong sulphuric acid, heat the liquid to 150°–160° C., and gradually add dry arsenic acid. When the reaction is over, the liquid is diluted with water and the precipitate separated and treated with a hot concentrated solution of alum, the liquid is filtered from the residue of unchanged alizarin, and the purpurin precipitated from the filtrate by adding hydrochloric acid.[1] The product may be purified by crystallisation from alcohol.

Purpurin crystallises from its solution in hot spirit in yellowish-red needles or prisms, containing $C_{14}H_5(OH)_3O_2 + H_2O$. It begins to sublime at 150° and melts at 153°, but is more readily decomposed by heat than is alizarin. In water, purpurin is more soluble than alizarin, and the solution in hot water free from alkali has a yellow colour. Purpurin also dissolves in alcohol and ether.

In caustic alkalies, purpurin dissolves easily with magenta or purple-red colour. It forms a compound with soda, which crystallises in well-defined long prisms. The alkaline solutions of purpurin become decolorised on prolonged exposure to light. On strongly acidulating a solution of purpurin in an alkali with hydrochloric-acid, purpurin hydrate is thrown down. The artificial purpurin paste probably consists chiefly of this body. When heated, it loses its water of hydration, and changes into ordinary purpurin. In warm alcohol it dissolves more readily than ordinary purpurin.

---

[1] The proportion of purpurin present in the commercial paste may be similarly determined by boiling the sample with a strong solution of alum or aluminium sulphate, filtering, precipitating the filtrate by hydrochloric acid and weighing the dried precipitate.

When heated with aqueous ammonia under pressure, purpurin is converted into purpurinamide, $C_{14}H_5(NH_2)(OH)_2O_2$. Owing to the formation of this body, an ammoniacal solution of purpurin, if kept for several weeks, loses its power of dyeing mordanted cloth. On neutralising the solution, the purpurinamide forms a dark crystalline precipitate, soluble in alcohol or a large quantity of hot water, but separating again on cooling in long crimson needles, which exhibit a deep green metallic reflection. It dissolves freely in fuming nitric acid (sp. gr. 1·5) at the temperature of boiling water, and on cooling the solution deposits magnificent scarlet crystals, which are insoluble in water, ether, and carbon disulphide, and only slightly soluble in alcohol.

With acetic anhydride, purpurin forms a triacetyl derivative of the composition $C_{14}H_5(OC_2H_3O)_3O_2$, which crystallises in yellowish needles fusing at 190°–193° C. An alcoholic solution of purpurin gives with alcoholic lead acetate a dark crimson precipitate, which dissolves on treatment with an excess of the reagent to form a fine crimson solution, the spectrum of which shows three absorption-bands. Alizarin when similarly treated gives a purple coloration or precipitate.

An alcoholic solution of purpurin gives with alcoholic copper acetate a dark reddish-yellow precipitate, whereas alizarin, if pure, gives a purple solution, but no precipitate, when treated similarly.

With lime and baryta water purpurin yields purple-red precipitates, and dyes cloth mordanted with alumina a colour varying from scarlet to dark red, without any shade of blue. Purpurin dyes cotton mordanted with ferric salts purple or black.

The most characteristic reaction of purpurin is its property of dissolving in a hot solution of alum with reddish-yellow colour and greenish-yellow fluorescence. The purpurin-alumina lake behaves similarly. The fluorescence is seen to perfection in a liquid prepared by adding a solution of purpurin in sodium carbonate to one of alum which has been previously treated with tartaric acid and sodium carbonate in quantity sufficient to prevent precipitation.

The absorption-spectrum of purpurin is characteristic. A solution of purpurin in alum or alkaline carbonate, if of suitable strength, gives two well-defined absorption-bands in the green, the less refrangible—situated above twice as far from line D as from line E[1]—being particularly sharp and black.[2] The absorption-spectrum of the solution of purpurin in carbon disulphide contains four nearly equidistant absorption-bands, of which the first, which is somewhat more refrangible than the D line, is the narrowest, the second and third broader, but very distinct, while the fourth is scarcely distinguishable from the general absorption. An ethereal solution of purpurin is faintly fluorescent, and shows a very dark narrow absorption-band slightly more refrangible than E, and a second wider and less defined band at F.

The detection of alizarin by a similar method is far less delicate, since alum cannot be used to separate it from the accompanying impurities, some of which produce absorption in that part of the spectrum in which all but the least refrangible of the absorption-bands occur, and this band is not the most intense or characteristic of those produced by alizarin (Stokes, *Jour. Chem. Soc.*, xii. 219).

To detect small quantities of alizarin in purpurin, a solution of the colouring matter in caustic soda should be exposed to the light till all the purpurin is destroyed. The liquid is then treated with dilute sulphuric acid and agitated with ether, alizarin being subsequently sought for in the evaporated ethereal solution.

$\left.\begin{array}{l}\text{ANTHRAPURPURIN}\\ \text{FLAVOPURPURIN}\end{array}\right\} C_6H_3(OH):C_2O_2:C_6H_2(OH)_2$ (see also page 263).

These two isomeric bodies differ from each other and from purpurin simply in the position occupied in the molecule by the hydroxyl groups. They are produced by fusing *beta*-anthraquinone-disulphonic acid and *alpha*-anthraquinone-disulphonic acid, respectively, with caustic soda and potassium chlorate (page 262). Both are valuable colouring matters, and exist in various brands of commercial alizarin. Anthrapurpurin is as important a colouring matter as alizarin itself, and used with it increases its brilliancy, while alone it gives very brilliant scarlet shades. *Alizarin for reds* consists chiefly of anthrapurpurin, while flavopurpurin gives yellower shades. Both colouring matters present a close resemblance to alizarin, and the general reactions of the commercial pastes are shown on page 276. In the following table, the principal distinctions between anthra- and flavo-purpurin are exhibited:—

---

[1] According to H. Morton, the refrangibility of the absorption-bands of a solution of purpurin in alum is sensibly affected by the temperature of the solution and the proportion of alum contained in it.

[2] By boiling a very small quantity of the root with alum, and observing the absorption-spectrum and fluorescence of the filtered liquid, Stokes detected purpurin in upwards of twenty species of the family *Rubiaceæ*, comprising the genera *Rubia*, *Asperula*, *Gallium*, *Crucianella*, and *Scherardia*.

	Anthrapurpurin.	Flavopurpurin.
Positions of the OH groups.	$\beta'1 : \alpha1 : \beta1$.	$\beta'2 : \alpha1 : \beta1$.
Appearance.	Orange needles; anhydrous.	Golden-yellow needles; anhydrous.
Solubility in alcohol.	Easily soluble in boiling alcohol.	Easily soluble even in cold alcohol.
Solubility in hot benzene.	Almost insoluble.	Soluble.
Solubility in boiling water.	Slight; solution turns red on prolonged boiling.	Slight; solution remains yellow after prolonged boiling.
Solubility in solution of alum.	Slightly soluble with orange colour on boiling; separates again on cooling.	Insoluble.
Colour of solution in strong sulphuric acid.	Dull violet colour, changing to fine red-violet on adding a trace of sodium nitrite.	Red-brown.
Colour of solution in caustic alkali.	Violet (but redder than an alkaline solution of alizarin); two absorption-bands simulating those of alizarin.	Purple (redder shade than with anthrapurpurin); on dilution, pure red. Two absorption-bands, more refrangible than those of alizarin, and a characteristic broad band in the blue.
Colour of solution in ammonia.	Violet; no absorption-bands.	Yellowish-red; no absorption-bands.
Colour of solution in sodium carbonate.	Violet.	Yellowish-red.
Reaction with alcoholic solution of lead acetate.	Purple precipitate, dissolving with violet colour on boiling with excess of the reagent.	Reddish-brown precipitate, dissolving very sparingly on boiling with excess of the reagent, with red colour.
Reaction with alcoholic solution of cupric acetate.	Fine violet colour.	Red coloration.

Anthrapurpurin and flavopurpurin are now met with in commerce in a state of almost perfect purity, but sometimes are very impure. G. Jellinek (*Ber.*, xxi. 2524; *J. S. C. Ind.*, vii. 743) states that the article supplied as pure flavopurpurin by various German alizarin makers sometimes contains as much as 30 per cent. of non-tinctorial substances, chiefly anthraflavic acid. For the detection of these impurities in commercial flavopurpurin, Jellinek recommends that the sample should be dissolved in alkali, and the solution treated with lead acetate. The precipitate is well washed with hot water, and decomposed by sulphuric acid in presence of alcohol. The colouring matter is then obtained from the alcoholic solution by fractional crystallisation.

Commercial Alizarin. Alizarin Paste.

Commercial alizarin always occurs in the form of an ochre-yellow or brownish-yellow paste, consisting of the solid colouring matters in a hydrated state mixed with a definite proportion of water.

Alizarin paste ordinarily contains 20 per cent. of solid matter. The strength is easily ascertained by drying a fair sample at 100° C. By exposure to this temperature the alizarin is rendered anhydrous, loses the slight solubility it previously possessed, and becomes wholly unfit for dyeing.[1] The *residue*, after drying, should be yellow,—not dark brown. After weighing, the residue should be ignited at a dull red heat. The *ash* obtained should not exceed 1 per cent. of the weight of the dried residue, and should be practically free from *iron*.

According to Benedikt and Knecht, commercial alizarin is liable to contain glycerin, turkey-red oil, and other thickening agents, for the detection of which they recommend dilution of the paste with water and filtration of the liquid, when a perfectly colourless filtrate should be obtained, which may contain small quantities of sodium chloride and other salts, but should leave no syrupy residue of glycerin on cautious evaporation. A practical objection to this method of examination exists in the great difficulty, sometimes amounting to impossibility, which attends the filtration of alizarin paste diluted with water. If the presence of glycerin or turkey-red oil be suspected, it would probably be preferable to examine the residue left on evaporating the paste to dryness at 100°.

Besides true alizarin, the commercial paste contains more or less of the dihydroxy-anthraquinones isomeric with alizarin, as well as several of the mono- and tri-hydroxyanthraquinones. All these bodies present a very close general resemblance to alizarin proper, but all except the trihydroxyanthraquinones (flavopurpurin and anthrapurpurin) are valueless as dyes, and these latter give very different shades from those produced by pure alizarin.

The following method is given by Benedikt and Knecht for recognising the constituents of commercial alizarin paste:—A small quantity of the sample is dissolved in a solution of sodium carbonate, and the liquid filtered. The residue consists of *anthraquinone* and *monohydroxyanthraquinone*, which may be separated by means of dilute caustic soda solution, in which only the latter is soluble. The filtered carbonate of sodium solution is acidulated with hydrochloric acid, and the precipitate boiled with milk of lime, which will dissolve any *anthraflavic* and *isoan-*

---

[1] The same statement applies to alizarin paste which has been frozen, and hence it is customary during severe weather to protect the colouring matter from the cold.

thraflavic acids with red colour.[1] On filtering and acidulating the filtrate these impurities will be reprecipitated, and may be collected, washed, and weighed. The insoluble lime-lake is removed from the filter and decomposed by agitation with dilute hydrochloric acid, and the separated colouring matter washed and weighed, or dissolved in ether and recovered by evaporating the ethereal solution. The residue thus obtained will contain the alizarin of the sample, mixed with any anthrapurpurin or flavopurpurin which may be present. According to Schunk and Römer, the detection and approximate determination of these three bodies in admixture can readily be effected as follows:—The mixture is dried at 100° C., and then placed between two glass plates, separated from each other by a leaden ring some millimetres in thickness. The whole is heated in an air-bath to 140°–150°, at which temperature the *alizarin* alone sublimes. On raising the temperature to 170°, a crystalline sublimate of mixed *flavopurpurin* and *anthrapurpurin* is obtained, the former of which assumes the shape of fine reddish-yellow needles, while the latter sublimes in compact, well-defined rhombic crystals. A separation of the two isomers may be effected by boiling with benzene, in which only flavopurpurin dissolves. (See also page 273).

---

[1] Both these bodies, as also monohydroxyanthraquinone, are valueless as dyes. Their presence in commercial alizarin may be detected by boiling the sample with milk of lime and filtering, when a yellow or brownish-red solution will be obtained. The following are the chief differences between these three allied substances:—

	β-Monohydroxy-anthraquinone.	Anthraflavic Acid.	Isoanthraflavic Acid.
Action of heat.	Sublimes, without melting, above 285°.	Melts above 330°, and sublimes.	Melts above 300°, and sublimes.
Action of water.	Easily soluble; insoluble in acidulated water.	Insoluble.	Insoluble.
Action of aqueous alcohol.	Separates from hot solution in yellow laminæ or needles.	Separates from solution in long, anhydrous, yellow needles or laminæ.	Separates from solution in hydrated crystals.
Action of hot, strong, sulphuric acid.	...	Forms yellow solution.	Forms deep red solution.
Action of cold baryta water.	Soluble with reddish-yellow colour.	Insoluble.	Easily soluble with dark red colour.
Action of hot lime water.	Soluble with reddish-yellow colour.	Slightly soluble, cold; nearly insoluble hot; solution yellowish-red.	Easily soluble with dark red colour.

Commercial Name.	Principal Constituent.	Colour of Paste.	Solubility in Water.	
			Cold.	Hot.
Alizarin P, V, V1, Ia, or No. 1.	Alizarin (page 264).	Ochre-yellow.	Insoluble.	Slightly soluble to yellow-red solution.
Alizarin YCA, X, G1, FA, SDG, 5RD, or No. 10.	Flavopurpurin (page 272).	Brownish-yellow.	Insoluble.	Very slightly soluble.
Alizarin SC (GD), RX, RF, 3RF, or SX extra.	Anthrapurpurin (page 272).	Brownish-yellow.	Insoluble.	Very slightly soluble.
Alizarin No. 6. Purpurin.	Purpurin (page 270).	Reddish-brown.	Slightly soluble.	Moderately soluble, with red colour.
Alizarin Orange, OR, OG, or N.	β-Mononitro-alizarin (page 267).	Brownish-yellow.	Insoluble.	Insoluble.
Anthracene Brown, Anthragallol.	Anthragallol (page 270).	Dark brown.	Insoluble (soluble in alcohol with yellow colour).	Insoluble.
Galloflavin.	$C_{13}H_6O_9$ (?).	Greenish-yellow.	Insoluble.	...
Alizarin Black.	Sodium bisulphite compound of naphthazarine.	Black.	Insoluble.	Soluble with red-brown colour.
Alizarin Blue.	Alizarin-quinoline (page 268).	Dark violet (or minute blue crystals).	Insoluble.	Insoluble.
Galleïn, Alizarin Violet, Anthracene Violet.	$C_{20}H_{10}O_7$ (page 78).	Violet (or dried lumps or crystalline powder of dark brownish-red or green colour).	Nearly insoluble.	Slightly soluble, with scarlet colour.
Ceruleïn, Anthracene Green, Alizarin Green.	$C_{20}H_8O_6$ (page 78).	Black.	Insoluble.	Insoluble.
Gallocyanin, Solid Violet.	$C_{15}H_{13}N_2O_5Cl$ (pages 74 and 259).	Greenish-grey (or when dry, bronze powder).	Insoluble.	Insoluble.

Colour of Solution in		Colour of Solution in strong Sulphuric Acid.	Colour on Cotton Mordanted with		
Dilute Caustic Soda.	Ammonia.		Alumina.	Iron.	Chromium.
Violet.	...	Yellowish-red; on dilution, orange-yellow precipitate.	Red.	Violet.	Puce or brown.
Red-violet (redder than anthrapurpurin).	Brown or yellowish-red.	Reddish-brown; on dilution, orange-yellow precipitate.	Red.	...	...
Violet (redder than alizarin I).	Reddish-violet.	Magenta or cherry red; on dilution, orange-yellow precipitate.	Red.	...	...
Magenta-red (redder than above brands).	Magenta-red.	Reddish-yellow; on dilution, reddish-brown precipitate.	Red (without blue shade).	Purple or black.	Red-brown.
Magenta-red.	...	Yellowish-brown; on dilution, yellow precipitate.	Orange.	Reddish-violet.	Reddish-brown.
Greenish-blue (or olive-brown).	...	Brownish-red; on dilution, brown precipitate.	...	...	Brown.
Dirty yellow or yellow-brown.	...	Reddish-yellow; on dilution, greyish-white precipitate.	...	...	Greenish-yellow.
Fine blue.	...	Dirty yellowish-green, changing to carmine-red on heating with evolution of SO_2; on dilution, brownish solution and black precipitate.	...	...	Black.
Greenish-blue (precipitated by large excess).	Greenish-blue.	Crimson-red; changing to yellowish-red on dilution.	Bluish-violet.	Greenish-blue.	India blue.
Fine indigo-blue, becoming dirty on standing, or reddish-violet on dilution.	Violet.	Reddish-yellow; unchanged on dilution.	Violet.	Black or green.	...
Grass-green.	Green.	Dirty yellowish-brown; on dilution, reddish-brown solution, and with more water a greenish liquid and greenish-black precipitate.	Green.	...	...
Reddish-violet.	...	Cornflower-blue; on dilution, magenta-red.	...	...	Deep bluish-violet.

The foregoing table (pages 276, 277) shows the characters of the different varieties of alizarin and analogous colouring matters met with in commerce in the form of paste.

Artificial alizarin does not contain purpurin, but in the natural product from madder more or less purpurin is usually present.

In forming an opinion on the quality of commercial alizarin, the performance of a miniature dye-test is very useful, and is best conducted as follows:—A piece of white calico, some feet in length and four inches wide, is boiled in water containing a little caustic soda, to remove any stiffening agents. After being thoroughly washed, it is immersed in a solution of aluminium acetate ("red liquor") of known measure and strength, the time of immersion and the temperature being duly noted. The calico is then removed, wrung out, and torn into a number of strips three inches wide, which are hung on a string to drain. 0·5 gramme of each sample of alizarin paste to be tested is then weighed out, and put into a corresponding number of wide-mouthed flasks or wide beakers of similar size arranged in a capacious water-bath. 1 litre of water at 40° C. is then poured into each, and the liquid well agitated to facilitate the solution of the alizarin. A strip of the previously mordanted calico is then immersed in the contents of each flask, care being taken that it is suspended freely so that all parts are in contact with the liquid. This is best done by attaching it to a thread tied to a glass rod placed across the mouth of the flask or beaker. The temperature of the bath is then gradually raised, so that it may reach 75° in about an hour and a half from the immersion of the cloth, after which the temperature is increased to about 90° C. for half an hour longer. The strips of calico are now withdrawn, rinsed in cold water, and dried. Each strip should then be cut into two equal portions, one of which is preserved between the leaves of a book or in other situation away from the light, while the others are steeped for half an hour at about 40°–42° C. in 1 litre of water containing 2 grammes of white curd soap.[1] The strips are then taken out, rinsed in cold water, and put into another bath made with the same quantities of soap and water, with the addition of 0·6 gramme of stannous chloride ("tin crystals"), which is allowed to boil for thirty minutes. The strips are then removed, well rinsed, dried, and preserved in the dark.

Instead of relying on the behaviour of the dye-stuff with a single mordant, it is preferable to use a piece of cloth printed in five or six parallel lines with, *e.g.* (*a*), strong solution of aluminium acetate; (*b*) weak aluminium acetate; (*c*) strong iron acetate; (*d*) weak iron acetate; (*e*) mixture of strong solutions of aluminium and iron acetates; (*f*) mixture of weak solutions of aluminium and iron acetates.[1]

---

[1] In some cases, as in the assay of reds, it is desirable to precede the soap treatment by an oil process. This consists in immersing the fabric in a 5 per cent. solution of turkey-red oil, again drying the cloth, and then exposing it to open steam in a suitable box for one hour.

The shades dyed by commercial alizarin depend much on the composition of the colouring matter. Thus the variety giving blue shades (*e.g.*, "*alizarin V*, or extreme blue shade") consists chiefly of real alizarin. In dyeing, it yields with alumina mordant a bluish but not very brilliant shade of red; but with a small proportion of mordant very beautiful shades of pink can be obtained. When mordanted with iron, it is used for dyeing and printing fast violets. The yellow shades of commercial alizarin (*e.g.*, alizarin GS) contain a large percentage of anthrapurpurin and flavopurpurin, and but little real alizarin. Anthrapurpurin yields an almost neutral red with alumina mordants; but flavopurpurin gives a fiery red containing a considerable proportion of yellow, and hence the larger the proportion of flavopurpurin the yellower the shade. Iron mordants give with anthrapurpurin and flavopurpurin violets of little or no practical value. Purpurin does not occur in artificial alizarin, but was a very common constituent of the dye from madder, which fact was the chief reason of the different shades produced by natural and artificial alizarin.

Detection of Alizarin and its Allies on the Fibre.

Alizarin and other allied colouring matters are applied in so many ways, and with such a variety of mordants, that it is not possible to describe the method of dyeing shortly. As the use of a mordant is essential, they are not so suitable for silk as the substantive coal-tar dyes. Alizarin is now used in wool-dyeing, not merely as a bottoming colour for indigo, &c., but as a self-colour with mordants. Thus when mordanted with alum and tartar it gives fine reds and scarlets; with stannous chloride, orange shades; with potassium bichromate, rich claret-browns; with ferrous sulphate, shades ranging from bluish-violet to black; with ammonio-sulphate of nickel, grey; and with uranium acetate, slate-blue shades. These colours are fast to light and air, and resist milling.

The mordants used in dyeing cotton with alizarin are various compounds of calcium, aluminium, iron, chromium and tin, besides tannic acid and oils. *Turkey-red*, one of the fastest and most perfect of the alizarin styles, is dyed by a complicated series of operations, in which the formation of a compound of alumina with alizarin and a fatty acid is an essential step. The method of operating is substantially that employed in the process of assay described on page 278. Treatment with ether changes cloth dyed turkey-red to a dull cherry-red colour, and on evaporating the ethereal solution a brilliant scarlet fat is left. This dissolves in hot caustic soda with purplish-blue colour, and on adding hydrochloric acid alizarin is precipitated in orange flakes. *Alizarin violet* may be obtained in a similar manner to turkey-red, the blue shade of alizarin being used for its production. Other violets are obtained by the use of an iron mordant.

---

[1] Pieces of cloth printed in the manner recommended, or any other which may be desired, can be obtained by order from many calico-printers.

Turkey-red is but little affected by a dilute solution of bleaching powder if free acid be absent, but the other alizarin colours are gradually bleached.

Alizarin is not affected by potassium bichromate, but free chromic acid destroys it. Dilute solutions of permanganate (1 per cent.) and alkaline solutions of ferricyanides are without effect on colours produced by artificial alizarin, but *purpurin* is easily oxidised. The last reagent especially is of value for distinguishing colours produced by artificial alizarin from those produced by madder, as the latter always contains purpurin. Madder-dyed fibres are also distinguished by boiling them with a strong solution of alum, when the purpurin is dissolved with formation of a reddish-yellow liquid, which exhibits a strong greenish-yellow fluorescence and characteristic absorption-bands (page 271).

On exposure to nitrous fumes, cloth dyed with alizarin-red becomes orange, from formation of nitro-alizarin.

Fibres dyed with alizarin are but little affected when boiled with ammonia or caustic soda solution of moderate strength. Alizarin red is turned to violet when boiled with baryta water. Dilute acids are almost without action. Concentrated hydrochloric acid decomposes the colour lakes, and partially or completely removes the metallic oxides. The violets are more readily affected than the reds, and of the latter turkey-red offers the greatest resistance.

Cold concentrated sulphuric acid dissolves the fibre of cotton as well as the colouring matter. On diluting the solution with water, the alizarin, &c., will be thrown down as a flocculent precipitate, which may be dissolved by agitation with ether. The separated ethereal solution on evaporation will leave a residue, in which alizarin and its associates may be recognised by their appearance on sublimation, the colour and absorption-spectra of their alkaline solutions, &c.

Fabrics dyed with alizarin are decolorised when boiled with a mixture of two parts of alcohol and one of strong hydrochloric acid. This reaction distinguishes *alizarin black* from *aniline black*, which latter colour is unaffected, or merely turned greenish, by similar treatment. *Logwood blacks*, on the other hand, are destroyed even by dilute acids, which acquire a red colour.

Strong acid oxidising agents, such as nitric acid and ferric chloride, destroy alizarin colours.

Chrysophanic Acid. $C_{15}H_{10}O_4 = C_{14}H_5(CH_3)(OH)_2O_2$. This substance, the nature of which was formerly misunderstood, is now recognised as a dihydroxy-methyl-anthraquinone, being homologous with chrysazin (page 263).

Chrysophanic acid occurs ready-formed in rhubarb root, senna leaves, the wall lichen (*Parmelia parietina*), and some other plants, or, at any rate, is readily produced by the oxidation of a substance pre-existing in these plants. This substance has the formula $C_{30}H_{26}O_7$, and is called chrysophan or chrysarobin, chrysophanic acid being a product of its oxidation, $C_{30}H_{26}O_7 + O_4 = 2C_{15}H_{10}O_4 + 3H_2O$. Many of the statements made as to the occurrence and properties of chrysophanic acid really apply to chrysarobin.

The best source of chrysophanic acid is the commercial product known as chrysarobin, or Goa powder,[1] which consists of the medullary matters of the stem and branches of *Andira araroba*, a plant growing in the neighbourhood of Bahia. The Goa powder is exhausted by boiling benzene or petroleum spirit, conveniently in a Soxhlet-tube. The filtered liquid, after concentration if necessary, deposits on cooling pale yellow, warty crystals. These may be purified by repeated crystallisation from glacial acetic acid, when the substance is obtained in small yellow laminæ.

Pure chrysophanic acid may be prepared from the chrysophan or chrysarobin obtained as above by pouring a somewhat dilute solution of caustic alkali over the substance contained in a large retort, and then passing a current of air over the surface of the liquid (Liebermann and Seidler, *Pharm. Jour.* [3], ix. 897). The retort is agitated so as to renew the surface, and the operation continued until the chrysarobin is dissolved, and the solution has acquired uniformly the red colour characteristic of an alkaline solution of chrysophanic acid. The liquid is then treated by an acid, and the precipitate washed, dried, and exhausted with petroleum spirit (not benzene) in a Soxhlet-tube. On cooling, the chrysophanic acid is obtained in beautiful yellow laminæ.

---

[1] In the *British Pharmacopœia* of 1885 the natural product Goa powder is confounded with the crystalline principle extracted therefrom by solvents, "*chrysarobinum*" being described as "medullary matter," and at the same time "minutely crystalline."

The following are the chief differences between chrysarobin and chrysophanic acid :—

	Chrysarobin.	Chrysophanic Acid.
Action of ammonia.	Insoluble.	Soluble with red colour.
Action of very dilute caustic potash solution.	Undissolved at first. On agitation with air, dissolves with red colour.	Soluble with red colour.
Action of strong caustic potash solution.	Soluble with yellow colour and strong green fluorescence. On exposure to air, colour changes rapidly to red.	Soluble with red colour.
Action of fusing caustic potash.	Brown coloration.	Blue coloration.
Action of concentrated sulphuric acid.	Soluble with yellow colour.	Soluble with red colour.

The chrysophanic acid of commerce consists of an indefinite mixture of chrysophan or chrysarobin with the true chrysophanic acid which is the product of its oxidation.

According to J. Agema, commercial chrysophanic acid may be purified by dissolving it in chloroform and adding an equal volume of rectified spirit, when the pure acid only is precipitated.

Chrysophanic acid crystallises in golden yellow scales or prisms. It melts at 162° C., and sublimes at a higher temperature with partial decomposition. Exposure to a temperature of 195° converts chrysophanic acid into a body allied to purpurin, which colours alum mordants pomegranate-red and iron mordants a light greenish-blue. It is nearly insoluble in water, but dissolves sparingly in hot alcohol (1 in 224), the greater part separating on cooling. Chrysophanic acid is also readily soluble in ether, chloroform, benzene, petroleum spirit, amylic alcohol, and glacial acetic acid, the solutions being yellow or brownish-yellow.

When treated with a solution of caustic alkali or ammonia, chrysophanic acid dissolves readily, forming a liquid which is pink when very dilute, and dark purplish-red in a more concentrated state. The chrysophanic acid is precipitated in yellow flakes on neutralising the alkaline liquid. A very small quantity of alkali suffices for the production of the red colour. If the red solution of chrysophanic acid in caustic alkali be evaporated to dryness, it turns violet and blue during the operation. The films deposited on the sides of the vessel especially exhibit this change of colour.

If a solution of chrysophanic acid in ether, chloroform, benzene, amylic alcohol, or petroleum spirit be shaken with solution of soda, the colouring matter passes completely or partially into the aqueous liquid, which it colours pink or crimson. Ammonia gives the same reaction as soda with a solution of chrysophanic acid in ether or petroleum spirit, but does not readily extract the colouring matter from its solution in chloroform or benzene.

The acid characters of chrysophanic acid are but feebly marked. It forms unstable barium and lead salts, which are decomposed even by carbonic acid. An ammoniacal solution of chrysophanic acid is precipitated lilac by acetate of lead and rose colour by alum.

Chrysophanic acid is not acted on by dilute nitric acid, but the strong acid converts it into tetranitro-chrysophanic acid, $C_{15}H_6(NO_2)_4O_4$, a body homologous with chrysamic acid, obtained by the action of nitric acid on aloes or chrysazin.

When heated with acetic anhydride and acetate of sodium, chrysophanic acid yields a diacetyl-derivative.

When heated with zinc-dust, chrysophanic acid is reduced to methyl-anthracene, $C_{15}H_{10}$, just as alizarin and chrysazin yield anthracene, $C_{14}H_8$, when similarly treated.

Chrysophanic acid possesses decided antiseptic properties, and has proved of service in the treatment of certain forms of skin-disease. It is said to be somewhat uncertain in its action, a fact which is not improbably due to an admixture of chrysarobin, to the deoxidising action of which impurity it has been suggested that the chrysophanic acid of commerce owes its chief value.[1]

Chrysophanic acid is said to produce purplish-brown stains on linen or cotton, which are only removable with difficulty, prolonged immersion of the fabric in a solution of bleaching-powder being the best mode of treatment. The author has not succeeded in producing these stains except in the presence of an alkali. A solution of chrysophanic acid in alcohol, acetic acid, or petroleum spirit merely colours linen a light yellow colour. On washing the stained fabric with soap, the purplish-brown stain is readily developed.[2]

An aqueous or alcoholic solution of chrysophanic acid does not dye silk or wool yellow.

---

[1] Working on this idea, Liebermann (*Pharm. Jour.* [3], xviii. 741, 780) has attempted to reduce chrysophanic acid to chrysarobin by treatment with zinc-dust and ammonia. He obtained instead a *leuco-derivative*, the lower homologue of which, prepared from alizarin and purpurin in a similar manner, is now commercially known as anthrarobin (page 266).

[2] Evidently, the production of chrysophanic acid stains on linen may be avoided by dissolving out the colouring matter and grease with benzene.

Chrysophanic acid is said to be liable to adulteration with picric acid and other yellow colouring matters. Inorganic admixtures may be detected by igniting a portion of the sample. *Picric acid*, if present, would be detected by the yellow coloration the sample imparts to cold water; by the yellow crystalline precipitate produced on adding potassium carbonate to the alcoholic solution of the sample; and by immersing a piece of white wool in the hot aqueous solution, which, in presence of picric acid, will be dyed yellow. *Aurin* or *rosolic acid* might be detected in chrysophanic acid by treating the sample with chloroform or benzene, which would dissolve the chrysophanic acid without affecting the admixture.

The extraction of the chrysarobin or chrysophanic acid present in plant-products may be effected by treating the powdered substance with the ether, benzene, or petroleum spirit, in the manner already described. Goa powder yields from 70 to 80 per cent. of the active principle, while the proportion of chrysophanic acid contained in rhubarb is but small. According to Dragendorff, the presence of chrysophanic acid in a condition (free) extractable by cold petroleum spirit is a test of the quality of rhubarb. Good rhubarb yields a colourless extract even when left for several days in contact with petroleum spirit, while a rhapontic rhubarb yields an intensely yellow extract. According to Rochleder (*Chem. News*, xx. 78), the acid from rhubarb generally contains emodin, $C_{15}H_{10}O_5$. This body has the constitution of a tri-hydroxymethyl-anthraquinone, and hence is homologous with purpurin. It occurs to a notable extent in the bark of *Rhamnus frangula*, and may be separated from chrysophanic acid by means of sodium carbonate, which dissolves the emodin only, with blood-red coloration. It forms long, brittle, monoclinic prisms, melting at 245°–250°, and is converted into methyl-anthracene by heating with zinc-dust.

A body having considerable analogy to chrysophanic acid occurs in the root of the Mexican plant *Trixis pipitzahuac* or *Perezia fructicosa*. This substance, which has been named pipitzahoic acid, has the formula $C_{15}H_{20}O_3$, and dissolves in alkalies with a colour resembling that of potassium permanganate (Anschütz and Leather, *Jour. Chem. Soc.*, xlix. 709).

SULPHURETTED AND UNCLASSIFIED COAL-TAR DYES.

Nearly all the coal-tar dyes of industrial importance have been described in one or other of the preceding sections. The chief exceptions are the remarkable sulphuretted dyes of the methylene blue class, discovered by Lauth.

Thio-Colouring Matters from Amido-bases.

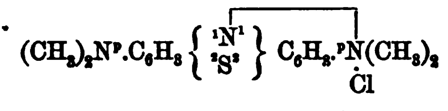
When the aromatic diamines are heated with sulphur, sulphuretted bases are formed, which yield violet colouring matters on oxidation. These bodies may be obtained more simply by passing sulphuretted hydrogen through the solution of the hydrochloride of the diamine, and then adding ferric chloride. The body thus obtained from para-diamidobenzene (para-phenylene-diamine) is known as

Lauth's Violet. $C_{12}H_{10}N_3SCl$. This curious colouring matter is the hydrochloride of the base thionine. It crystallises from a faintly acid solution in thin prismatic needles, having a beetle-green lustre. It dissolves slightly in cold but more readily in hot water, to form a solution which appears violet-red by transmitted, and violet-blue by reflected light. It is almost entirely precipitated from its aqueous solution by strong hydrochloric acid, but on adding excess redissolves with fine dark blue coloration. By precipitating a solution of Lauth's violet with soda or ammonia, the free base, $C_{12}H_9N_3S$, may be obtained as a brownish-red or black crystalline precipitate, or from a hot solution in small needles with a feeble green reflection. Thionine dissolves only slightly even in hot water, but more readily in alcohol, to a reddish-violet solution, which exhibits a fine brownish-red fluorescence.

Thionine and its salts dissolve in strong sulphuric acid with fine yellowish-green colour, changing to blue and violet on dilution with water. In this reaction thionine exactly resembles the safranines (page 254).

Lauth's violet is not employed in practice, but the important colouring matter known as *methylene blue* has the constitution of a tetramethyl-thionine hydrochloride.

Methylene Blue. $C_{16}H_{18}N_3SCl$. This colouring matter may be represented by the following formula :—



$$(CH_3)_2N^p.C_6H_3\left\{\begin{matrix}{}^1N^1\\{}^2S^2\end{matrix}\right\}C_6H_3.{}^p\underset{Cl}{N}(CH_3)_2$$

It may be prepared by treating dimethyl-aniline hydrochloride with sodium nitrite, and then with sulphuretted hydrogen until the solution loses its yellow colour and is covered with a blue scum, when ferric chloride or bichromate of potassium is added till the smell of sulphuretted hydrogen has disappeared. The liquid is then saturated with common salt and zinc chloride added. The precipitate is separated, redissolved in water, and again precipitated with salt and chloride of zinc. The product so obtained in the *double zinc salt*. From it the chloride may be prepared by adding strong hydrochloric acid to the concentrated solution. Methylene blue may also be obtained from helianthin in the manner described on page 211,[1] and by various other reactions.

Methylene blue occurs in commerce as a hydrochloride, but more frequently as the double zinc salt. It forms a dark blue or reddish-brown powder with a bronze reflection. In water or alcohol it dissolves easily with blue colour. The solution is unchanged or turned greenish by hydrochloric acid. Caustic soda changes the colour to violet, and the addition of strong alkali to a concentrated solution produces a dirty blue or violet-black precipitate. In concentrated sulphuric acid, methylene blue dissolves with grass-green colour, which, on addition of water, becomes first blue and then violet.

From a solution of commercial methylene blue, the iodide, $C_{16}H_{18}N_3SI$, is completely precipitated on adding iodide of potassium, and potassium bichromate also completely precipitates the solution as a purple-violet chromate. Methylene blue forms a soluble compound with tannin which is taken up by metallic mordants.

Tetramethylthionine Hydroxide, $C_{16}H_{18}N_3S.OH$, the free base of methylene blue, is most readily obtained by treating a solution of the iodide or chloride with freshly precipitated argentic oxide. On evaporating the filtered liquid *in vacuo*, the base is obtained as a dark amorphous mass which acquires a green metallic lustre when rubbed, forms a syrupy solution in water, and dissolves readily in alcohol. The solution decomposes various metallic salts, like an alkali, but is very unstable.

By treating methylene blue with zinc and acetic acid, or with an alkaline solution of sodium hyposulphite, the leuco-derivative, $C_{16}H_{19}N_3S$, is obtained. This body crystallises from ether in flat satiny needles, having a penetrating odour resembling that of the lobster. It is readily soluble in water, and is extremely oxidisable both in the dry state and in solution, methylene blue and other products being formed. In acid solution, tetramethylleucothionine is more stable, and it forms a readily soluble and crystallisable double zinc salt.

The formation of methylene blue affords the most delicate and certain reaction for the detection of sulphuretted hydrogen in neutral or acid solution, far exceeding in this respect the reactions with lead salts and nitroprussides. 100 c.c. of the liquid to be tested should be treated with 2 c.c. of fuming hydrochloric acid, and a few grains of dimethyl-paradiamido-benzene sulphate (page 211) added. On then adding a drop or two of ferric chloride solution, methylene blue will be formed either immediately or on standing, if any sulphuretted hydrogen was previously present.

---

[1] Mention of the last stage of the process, namely, oxidation of the reduced product by ferric chloride, is accidentally omitted on page 211.

Methylene blue is a valuable dye for cotton yarn and calico-printing. The blue produced has a greenish shade, especially in artificial light. The colour is faster than aniline blue, being unaffected by light and unacted on by neutral soap solution or dilute hypochlorites. Ammonia is also without action, but alkaline soaps and caustic alkalies remove the colour. On treating the fabric with hydrochloric acid, it is turned green and the dye is gradually removed, the acid liquid remaining green. Stannous chloride and other reducing agents discharge methylene blue more rapidly than other blue dyes. A three per cent. solution of potassium bichromate changes a fabric dyed with methylene blue to violet, and finally discharges it. If the dye was mordanted with tannin, a dark brown colour remains.

The behaviour of methylene blue with reducing agents and the sensitiveness of the resultant leuco-derivative render the colouring matter of great value in bacteriological research. "The bacilli of tuberculosis, glanders, and cholera were first discovered by the aid of methylene blue."

Ethylene Blue closely resembles methylene blue, but is prepared by using diethyl-aniline instead of the lower homologue.

Methylene Red, $C_{16}H_{18}N_4S_4,2HCl$, is a secondary product obtained in the formation of methylene blue, especially if the treatment with sulphuretted hydrogen be too prolonged and much ferric chloride be used. It remains in the mother-liquor when the blue is precipitated by the addition of salt. It is decolorised by alkalies and reducing agents, and turned blue by oxidising agents. A modified methylene blue is obtained from it in practice by treating the acid solution first with zinc-dust and then with ferric chloride.

Unclassified Coal-Tar Dyes.

Of the coal-tar dyes not falling naturally into any of the groups already considered, the following are all which require special description.

Aldehyde Green. $C_{22}H_{27}N_3S_2O$. This colouring matter, now practically obsolete, is of interest as being one of the first green dyes obtained from aniline. It was prepared by the reaction of aldehyde on magenta and treatment of the product with sodium thiosulphate (hyposulphite). It formed an amorphous green powder, insoluble in water and but little soluble in alcohol, but readily soluble in a mixture of alcohol, water, and sulphuric acid.

Canarin. $C_3N_3S_3H$. This colouring matter, sometimes called *persulphocyanogen yellow*, is not strictly a coal-tar dye, as it is produced by the action of an oxidising agent, such as chlorine or nitric acid, on a thiocyanate (sulphocyanide). It will be considered at greater length in the chapter on "Cyanogen Compounds." Canarin forms an orange-yellow powder insoluble in water, alcohol, or ether. It dissolves in alkalies with yellow colour, and on addition of hydrochloric acid is reprecipitated from the solution in orange-yellow flocks. It dissolves in strong sulphuric acid, but is reprecipitated on adding water. It is employed in calico-printing.

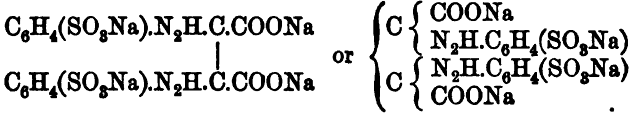
Thiorubin, a colouring matter made by Dahl & Co., is the sodium salt of thio-paratoluidine-azo-betanaphthol-disulphonic acid:—$NH_2.C_6H_3(CH_3).S.C_6H_3(CH_3).N_2.C_{10}H_4(OH)^{\beta}(SO_3Na)_2$. It occurs as a reddish-brown powder, soluble in water with magenta-red colour. Hydrochloric acid precipitates the solution yellowish-brown, while soda turns it bluer. In strong sulphuric acid thiorubin dissolves with magenta-red colour, the solution giving a yellowish-brown precipitate on dilution with water. An acid solution of the dye gives a red on wool.

Curcumin S, called also *sun-yellow* and *maize*, is the sodium salt of the disulphonic acid of azoxy-stilbene, and has the following formula:—

$$\left\{\left\{\begin{matrix} CH : C_6H_3(SO_3Na).N \\ CH : C_6H_3(SO_3Na).\dot{N} \end{matrix}\right\}\right. O$$

Curcumin S is prepared by heating paranitrotoluene-sulphonic acid with caustic soda, and occurs in commerce as a brown powder, soluble in water with brownish-yellow colour. The solution in strong sulphuric acid is violet, but becomes yellow on moderate dilution with water. Curcumin dyes silk and wool reddish-yellow in an acid bath.

Tartrazin is a body of peculiar composition. It has the constitution of a sodium salt of diazotartaric-acid-diphenylhydrazine-disulphonic acid (or diphenyl-parasulphonic-acid-osazon-dioxytartaric acid).



$$\begin{array}{l} C_6H_4(SO_3Na).N_2H.C.COONa \\ \qquad\qquad\qquad\qquad\quad | \\ C_6H_4(SO_3Na).N_2H.C.COONa \end{array} \quad \text{or} \quad \left\{\begin{array}{l} C\left\{\begin{array}{l} COONa \\ N_2H.C_6H_4(SO_3Na) \end{array}\right. \\ C\left\{\begin{array}{l} N_2H.C_6H_4(SO_3Na) \\ COONa \end{array}\right. \end{array}\right. .$$

Tartrazin is prepared by the action in alkaline solution of two molecules of phenylhydrazine-parasulphonic acid on one of dioxytartaric acid (*Jour. Soc. Chem. Ind.*, v. 427). It forms a beautiful orange-yellow powder, soluble in hot water to a golden-yellow solution, which if concentrated deposits a yellow precipitate on cooling. On adding alcohol to the concentrated aqueous solution a crystalline precipitate is obtained. The solution is not changed by dilute acids, but becomes reddish on adding caustic soda. Stannous chloride produces a yellow precipitate, soluble in oxalic acid. Barium chloride gives a yellow precipitate, but calcium chloride occasions no change. Concentrated sulphuric acid dissolves the solid dye with yellow colour, which is unchanged on dilution. Tartrazin precipitates the coal-tar bases very completely (W. R. Richardson, *Jour. Soc. Dyers, &c.*, iii. 2), and dyes wool yellow in an acid bath.

Various other dyes from hydrazines have been recently patented (*Jour. Soc. Dyers, &c.*, iii. 132, iv. 109). Thus *isatin-yellow* is obtained by the action of isatin on phenylhydrazine-parasulphonic acid, and *phenanthrene-red* by the reaction of one molecule of phenanthrenequinone on two of naphthylhydrazine-sulphonic acid.

BENZOFLAVINE is the typical member of a series of basic dyestuffs obtained by the reaction of one molecule of benzaldehyde on metatoluylene-diamine (or other aromatic meta-diamine) and one of its hydrochloride or sulphate. The product, $C_{21}H_{24}N_4,2HCl$, consisting of the hydrochloride of tetramido-ditolylphenylmethane, is heated with hydrochloric acid under pressure, when the hydrochloride of hydrodiamido-dimethyl-phenylacridine, $C_{21}H_{21}N_3$, is obtained, with elimination of ammonia. On exposure to air or treatment with an oxidising agent of moderate power, such as ferric chloride, this body is oxidised to diamido-dimethyl-phenylacridine or *benzoflavine* (compare page 246). The new colouring matter is a yellow substance soluble with difficulty in cold water, but more readily on heating. It is precipitated from its aqueous solution by dilute acids. In strong sulphuric acid it dissolves with yellow colour and pronounced yellowish-green fluorescence. The alcoholic solution shows an intense yellowish fluorescence, which disappears on the addition of an acid. The free base of benzoflavine is colourless and insoluble in water, but soluble in alcohol and ether.

COLOURING MATTERS OF NATURAL ORIGIN.

The dyes occurring naturally in animal or vegetable products, or which can be produced therefrom by comparatively simple means, are very numerous and interesting; and there is no doubt that the methods for their extraction or production would have been greatly improved of late years had not the coal-tar dyes engrossed the attention of nearly all investigators actively interested in the chemistry of colouring matters. The use of some of the natural colouring matters has greatly decreased, owing to the rivalry of the coal-tar dyes, and the production of some of them is nearly, if not wholly, a thing of the past. Thus the azo-scarlets have greatly diminished the consumption of cochineal, while artificial alizarin has nearly extinguished the natural dye from madder; and alizarin-blue and the indulines now compete with indigo, which is itself producible by complex synthetical processes from the coal-tar constituent toluene, C_7H_8.

The dyes and colouring matters of natural origin may be conveniently classified under the following heads:—

INDIGO, and allied colouring matters.
LICHEN DYES, such as orchil, cudbear, litmus.
RED DYES FROM WOODS, &c., as Brazil-wood and logwood.
YELLOW VEGETABLE DYES, such as saffron, turmeric, weld.
CHLOROPHYLL and its allies; and
ANIMAL DYES, such as cochineal.

Of the colouring matters included in the above arrangement, *madder* has already been referred to under the heads of alizarin and purpurin (pages 264, 270); *chlorophyll* and many other plant-colours receive little or no practical application, and hence need not be specially described; while the colouring matters of blood, bile, urine, &c., will be better considered in the sequel.

Indigo.

Indigo is the product of various species of leguminous plants of the genus *Indigofera*,[1] which appear to be indigenous in Cambay, but are also cultivated in India, China, Java, and other parts of the East. It is also grown in the West Indies and South America, and the species *Indigofera argentea* is cultivated in Egypt and Arabia.

Indigo does not exist ready-formed in the above plants, but is produced by the decomposition of a glucoside called indican, $C_{26}H_{31}NO_{17}$, which may be extracted from them by cold alcohol.

---

[1] The most valued and extensively cultivated species is the *Indigofera tinctoria*, but *I. disperma*, *anil*, and *argentea* are also widely grown. Less important species are *I. hirsuta*, *pseudo-tinctoria*, *sericea*, *cytisoides*, *angustifolia*, *triplia*, *glabra*, *glauca*, &c. *Indigofera tinctoria* is grown from seeds, and is a herbaceous plant with a single stalk, growing to a height of 3 feet or a little more, and about the size of the finger. The value of the crop is almost in proportion to the abundance of leaves, as the colouring matter exists chiefly in that part of the plant.

To obtain indigo from the plants, the chopped leaves or twigs are completely covered with water. Fermentation sets in, and continues from nine to fourteen hours, according to the temperature. When complete, the water is run off into shallow vats, where it is subjected to agitation to expose it to the air.[1] The yellow liquid thereby assumes a greenish colour, and the indigo separates in flakes. After standing for an hour, the blue pulpy indigo is separated, and boiled with water to prevent secondary fermentation and the consequent formation of objectionable brown products. After standing twenty-four hours, the liquid is again boiled, and then passed through a coarse filter. The precipitate is separated, pressed, and dried slowly in sheds, from which the light is carefully excluded.[2]

The indigo thus obtained varies greatly in quality, both as respects the proportion of blue colouring matter it contains and in its freedom from objectionable impurities (see page 302).

Indigo may also be obtained from several plants besides the *Indigofera*, but these are more generally used directly for dyeing blue than for extracting the indigo. The most important of these indigo-yielding plants are *Isatis tinctoria* or woad, once extensively cultivated both in England and on the Continent; *Polygonum tinctorium* and *Nerium tinctorium; Asclepias tingens; Eupatorium tinctorium*, one of the Compositæ; and several species of orchids, which, when cut, become blue at the section after exposure to the air.

Woad or *pastel* is a biennial cruciferous plant. The leaves, of which two crops are yielded, are gathered in the second year, and are rapidly washed and dried. They are used directly for dyeing, or are made into a paste with water, piled in heaps, allowed to ferment for fourteen days, and then made into small balls and dried. The product is sometimes again moistened with water and subjected to a second fermentation, during which ammonia is evolved. The best woad comes from France. The balls are light, of a green or yellowish-green colour, and have a sickly odour. When cut, woad should exhibit a soft, shining surface, and when rubbed on paper should leave a green mark. It improves by keeping, and some manufacturers consider that the finest shades of indigo-dyeing cannot be obtained without an admixture of woad.

---

[1] Some manufacturers add a little lime-water at this stage, while J. Sayers recommends the addition of ammonia during the fermentation. By this means the yield of colouring matter may be increased fully 100 per cent. (*Jour. Soc. Dyers, &c.*, ii. 141).

[2] The best qualities of indigo are usually those manufactured by Europeans, who operate with more care than the natives.

Isatis indigotica is cultivated in some parts of China for the preparation of a variety of indigo which is sold in the form of paste. When dried it appears blackish, and is used in producing *Canton blue*, &c.

Polygonum tinctorium is also indigenous to China, and yields an indigo of superior quality. It is also used for dyeing directly. The attempts made to acclimatise the plant in Europe have been unsuccessful.

A substance allied to indican sometimes occurs in urine, and gives rise, by its conversion into indigo-blue, to a blue coloration of the liquid when left in contact with the air, or when treated with sulphuric acid.

INDICAN, $C_{26}H_{31}NO_{17}$, already referred to as the natural glucoside by the decomposition of which indigo-blue is produced, was first isolated by E. Schunck.[1] It forms a transparent brown syrup, from which it is impossible to separate the water without causing decomposition. The aqueous solution has a yellow colour, bitter taste, and slight acid reaction. When boiled with caustic alkali it evolves ammonia. Weak solutions of alkalies and lime water produce a bright yellow colour. The alcoholic solution of indican gives a bright yellow precipitate with lead acetate, which is increased on adding ammonia; but the aqueous solution does not give this reaction. Indican is soluble in ether, but is extracted by water from its ethereal solution.

The most characteristic and important property of indican is the behaviour of its solution with dilute acids, by the action of which it splits up with formation of indigotin or indigo-blue, indirubin, and indiglucin. The reaction occurs slowly in the cold, but rapidly at a boiling heat, the liquid becoming first sky-blue, then opalescent, and finally purple, and on cooling a purple deposit of mixed indigotin and indirubin is obtained (both of which may be obtained in a crystalline state by sublimation), while indiglucin remains in solution. The following formula represents the formation of indigotin from indican:—

---

[1] Schunck has described the following process for the preparation of indican:—Dried woad leaves are finely powdered and extracted with alcohol by percolation. A little water is added, and the solution concentrated as quickly as possible at the ordinary temperature in a current of air. The residual brown liquid is filtered from the green residue of fat and colouring matter, and agitated with some freshly precipitated cupric hydroxide. The liquid is filtered, the copper precipitated by sulphuretted hydrogen, and the liquid again filtered. The filtrate, which should be light yellow, is concentrated to a syrup at the ordinary temperature in a current of air, treated with cold alcohol to remove decomposition-products, filtered, and mixed with twice its measure of ether. The filtered liquid yields on evaporation a clear brown syrup consisting of pure indican.

$$\underset{\text{Indican.}}{C_{26}H_{31}NO_{17}} + 2H_2O = \underset{\text{Indigotin.}}{C_8H_5NO} + \underset{\text{Indiglucin.}}{3C_6H_{10}O_6}.$$

Indigotin or indigo-blue is considered more at length on page 294.

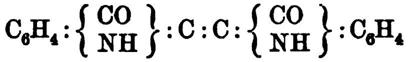
INDIGO BROWN. If an aqueous solution of indican be boiled or heated for some time it undergoes a change, and on now treating it with an acid it yields neither indigotin nor indirubin, but dark brown or blackish flocks, consisting of a mixture of two brown resinous bodies, called by Schunck indiretin and indihumin, of which only the latter is soluble in alcohol, and to which bodies he attributes the formula $C_{18}H_{17}NO_{10}$ and $C_8H_8NO_5$ respectively.

Leucine, $C_6H_{13}NO_2$, a body produced in the putrefaction of cheese, and by the treatment of various animal substances with sulphuric acid, is also a product of the reaction of dilute acids on indican.

INDIRUBIN or Indigo Red, C_8H_5NO, is obtained with indigotin by the decomposition of indican, especially when oxalic or tartaric acid is used. It may be separated from the indigotin by boiling the precipitate with alcohol. On concentrating and cooling the alcoholic solution, the indirubin is obtained in long red crystals, insoluble in caustic alkalies, but reducible by boiling with an alkali and stannous chloride or glucose to a leuco-derivative, the solution of which on exposure to air yields purple flakes, which when washed, dried, and heated, give a sublimate of beautiful needles, readily soluble in boiling alcohol, and recrystallising as the solution cools. If a piece of calico be immersed in a reduced alkaline solution of indirubin, and then exposed to the air, it becomes dyed a fast purple colour (not blue as with indigotin) which is not affected either by acids or soap. Indirubin dissolves in cold concentrated sulphuric acid with beautiful purple colour. On heating the solution it becomes lighter and gives off a little sulphur dioxide. On diluting the solution of indirubin in sulphuric acid with water, a liquid is obtained which dyes cotton, wool, and silk a fine purple colour. Indirubin is not affected by boiling with dilute sulphuric acid and potassium bichromate, a character which distinguishes it from indigotin.

INDIGLUCIN, $C_6H_{10}O_6$, is obtained from the liquid from which the above colouring matters have been separated, by adding excess of lead acetate, filtering, and treating the filtrate with excess of ammonia. The bulky yellow precipitate thus obtained is decomposed by sulphuretted hydrogen, and the indiglucin purified by repeating the process or treatment with animal charcoal. On concentrating the colourless liquid or syrup, and adding alcohol and two volumes of ether, the indiglucin separates as a pale yellow, sweetish syrup, which turns red and blackens when heated with sulphuric acid, and yields oxalic acid on treatment with nitric acid. It reduces hot Fehling's solution and silver nitrate. The solution gives no precipitate either with neutral or basic lead acetate, unless ammonia be added. If milk of lime be added and the solution filtered, a strongly alkaline liquid is obtained, and on boiling this it becomes thick from the formation of a flocculent yellow precipitate, which completely redissolves to a clear yellow solution on cooling. This reaction may be repeated indefinitely. By fermentation with yeast, indiglucin appears to yield acetic acid.

INDIGOTIN. INDIGO BLUE. C_8H_5NO or $C_{16}H_{10}N_2O_2$. This substance probably has the constitution represented by the following formula:[1]—



$$C_6H_4:\left\{\begin{matrix}CO\\NH\end{matrix}\right\}:C:C:\left\{\begin{matrix}CO\\NH\end{matrix}\right\}:C_6H_4$$

Indigotin is the constituent on which the value of commercial indigo depends. Besides the natural product as contained in indigo, indigotin may be obtained from coal-tar by a series of complex reactions described on page 33. The artificial indigo thus obtained, or rather the phenyl-propiolic acid which yields indigotin on reduction, was recently an article of commerce, but it has not been found possible to produce it at such a price as would enable it to compete successfully with the natural product.

Pure indigotin may be obtained by mixing one part of commercial indigo in fine powder with two parts of plaster of paris, making the whole into a paste with water, and spreading it on an iron plate. When quite dry the mass is cautiously heated, when the surface becomes covered with beautiful crystals of pure indigotin, which may be removed with a fine spatula. Indigotin may also be obtained in a pure state by the oxidation of indigo-white, $C_{16}H_{12}N_2O_2$ (page 296), or indoxylic acid, $C_9H_7NO_3$, or by the reduction of orthonitro-phenyl-propiolic acid (page 33). It may also be prepared by heating isatin, $C_8H_5NO_2$, with a mixture of phosphorus trichloride and pentachloride, and reducing the resultant isatic chloride, C_8H_4NOCl, by ammonium sulphide.

---

[1] Baeyer regards the molecule of indigotin as composed of two symmetrical halves, $C_6H_4\left\{\begin{matrix}CO\\NH\end{matrix}\right\}C:$, and this half-molecule he calls indogen. The indogenides are compounds of yellow or bluish-red colour, and some of them yield blue salts which exhibit the indigo spectrum.

Pure indigotin forms dark blue crystals exhibiting a coppery reflection and having the form of a right rhomboidal prism. In the form of powder it is deep blue, and assumes a coppery lustre when burnished. Its specific gravity is 1·35. Indigotin is not fusible, but sublimes at about 290° C., with more or less decomposition. In an inert gas it may be volatilised unchanged.

Indigotin is unchanged in the air at ordinary temperatures, and has neither taste nor smell. It is insoluble in hot or cold water, cold alcohol, ether, and fatty and essential oils. Creosote, carbolic acid, absolute alcohol, amylic alcohol, and carbon disulphide dissolve a little indigotin when hot, but it is again deposited on cooling. Its best solvents are glacial acetic acid, nitrobenzene, and aniline. On boiling powdered indigo with aniline it readily dissolves to form a blue solution, which if filtered hot and allowed to cool deposits nearly all the indigotin in beautiful crystals, which after being washed with alcohol are perfectly pure. Boiling paraffin and high boiling petroleum are also solvents of indigotin. The dilute solutions have the colour of an alcoholic solution of magenta.

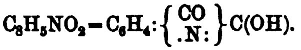
If a little finely powdered indigotin be treated with glacial acetic acid and one or two drops of strong sulphuric acid added, a deep blue solution is formed, from which the indigotin is precipitated unchanged on dilution with water. If any fibre be immersed in the undiluted solution, and then washed with water, it will be dyed blue.

Indigotin is a perfectly neutral substance, and is insoluble in dilute acids and alkalies.

When subjected to dry distillation, either alone or in admixture with an alkali, indigotin yields *aniline*, C_6H_7N.

When subjected to the action of oxidising agents, such as dilute nitric acid, chromic acid, or chlorine, indigotin is converted, in the presence of water, into a body called *isatin*[1] or *indigotic acid*.

---

[1] ISATIN, 
$C_8H_5NO_2 = C_6H_4{:}\left\{\begin{matrix}CO\\ .N{:}\end{matrix}\right\}C(OH)$. This body is obtained by oxidising indigo by chromic acid, or preferably nitric acid. Powdered indigo is made into a thin paste with water, the mixture heated to the boiling point, and nitric acid added cautiously till the blue colour disappears, when the whole is largely diluted with boiling water and the liquid filtered. Impure isatin separates on cooling, and is washed with ammoniacal water. Isatin forms deep yellowish-red prismatic crystals, sparingly soluble in cold water, but freely in boiling water and in alcohol. The solution stains the skin yellow, and gives it a disagreeable odour. When heated, isatin melts and sublimes, with partial decomposition. It forms crystalline compounds with the acid sulphites of the alkali-metals, and dissolves in alkalies to form violet solutions, which turn yellow when heated and then contain a salt of *isatic acid*. *Hydrindic acid* or *dioxindole* is formed by the action of

Hot and strong nitric acid converts indigo-blue into picric and nitrosalicylic acids, some carbonic or oxalic acid being simultaneously formed.

HYDRINDIGOTIN. INDIGO WHITE. REDUCED INDIGO. $C_{16}H_{12}N_2O_2$. When indigotin is subjected to the action of reducing agents it assimilates two atoms of hydrogen, forming a leuco-body of the above composition, the constitutional formula of which is probably:—

$$C_6H_4\left\{\begin{matrix}CO\\NH\end{matrix}\right\}CH\,.\,HC\left\{\begin{matrix}CO\\NH\end{matrix}\right\}C_6H_4$$

A great variety of substances have the power of reducing indigo-blue to indigo-white. Thus in alkaline solution, or presence of free alkali, we may use:—sodium amalgam; zinc, tin, aluminium, and phosphorus; ferrous hydroxide; phosphorous, hypophosphorous, and hyposulphurous (Schutzenberger's) acids; certain phosphides, arsenides, and sulphides (especially sulphide of arsenic); glucose, gallic acid, the butyric ferment, &c. The resultant reduced indigo is soluble in the alkaline liquid. In acid solutions, indigotin is

sodium amalgam on this solution. Further reduction in acid solution produces oxindole, and this when distilled with zinc-dust yields indole, a weak base existing in human excrement. The relationship of these bodies to indigotin, isatin, and each other is shown by the following constitutional formulæ:—

Hydrindigotin, ...	$C_6H_4\left\{\begin{matrix}.CO.\\.NH.\end{matrix}\right\}CH.HC\left\{\begin{matrix}.CO.\\.NH.\end{matrix}\right\}C_6H_4$
Indigotin, ...	$C_6H_4\left\{\begin{matrix}.CO.\\.NH.\end{matrix}\right\}C{:}C\left\{\begin{matrix}.CO.\\.NH.\end{matrix}\right\}C_6H_4$
Isatin, ...	$C_6H_4\left\{\begin{matrix}.CO.\\.N:\end{matrix}\right\}C(OH)$
Isatic acid, . . .	$C_6H_4\left\{\begin{matrix}.CO.CO.OH\\.NH_2\end{matrix}\right.$
Dioxindole, . . .	$C_6H_4\left\{\begin{matrix}.CH(OH).\\.NH.\end{matrix}\right\}CO$
Oxindole, ...	$C_6H_4\left\{\begin{matrix}.CH_2.\\.NH.\end{matrix}\right\}CO$
Indole, ...	$C_6H_4\left\{\begin{matrix}.CH:\\.NH.\end{matrix}\right\}CH$

Silver nitrate throws down from alkaline solutions of isatin a red precipitate containing $C_8H_4AgNO_2$. The hydrogen of the hydroxyl group may also be replaced by acid radicals, as in acetyl-isatin, $C_8H_4(C_2H_3O)NO_2$. Mono- and di-chlor- and brom-isatins are obtained by the action of chlorine and bromine on isatin or moist indigo. Isatin-sulphonic acid, $C_8H_4(SO_3H)NO_2$, is formed by the treatment of indigotin-sulphonic acid by permanganate or other oxidising agents in acid solution. It is soluble, and difficultly crystallisable.

reduced less readily, hyposulphurous acid (H_2SO_2) being almost the only available agent.[1]

Hydrindigotin is a greyish-white, amorphous, tasteless, odourless substance, having a silky lustre. Heated out of contact with the air a small quantity of indigotin sublimes, and a carbonaceous mass is left. In contact with the air at the ordinary temperature white indigo gradually becomes blue from oxidation, and the action is rapid in presence of moisture. Indigo-white is insoluble in water and dilute acid liquids, but dissolves in alcohol and ether.

Hydrindigotin is soluble in solutions of the alkalies and alkaline earths, but its acid characters are very feebly marked, for the presence of a textile fabric suffices to decompose its compounds, the indigo-white uniting with the fibre and alkali being set free.[2] The alkaline solutions of reduced indigo have a yellow tint, but in contact with air they become green and blue and covered with a bronzy scum, and deposit minute crystals of indigotin. Addition of an oxidising agent produces the same effect more rapidly, and even a slight rise of temperature causes a similar change. The application of indigo in dyeing by the vat-process is based on its reduction to white indigo, the solubility of the reduced substance in alkaline liquids, and its reoxidation to indigo-blue on exposure to air.[3] Alkaline solutions of hydrindigotin gives bulky white precipitates with solutions of magnesium, zinc, aluminium, lead, ferrous, manganous, and stannous salts. The last precipitate is employed for printing indigo on fabrics. When heated it yields metallic tin and a sublimate of indigotin.

---

[1] A convenient process for the preparation of white indigo consists in treating 1 part indigo-blue with 3 parts of crystallised ferrous sulphate, 3 parts of slaked lime, and 20 of water in a closed vessel. The mixture is agitated at intervals for some days, and finally allowed to settle. The pale yellow liquid is then syphoned off into a bottle filled with carbon dioxide, containing some recently boiled hydrochloric acid. The indigo-white is immediately precipitated, and when the bottle is quite full it is immediately closed. After standing some time the liquid is filtered in an atmosphere of carbon dioxide or coal-gas, the precipitate washed with air-free cold water, and dried *in vacuo*.

An alternative process is to treat the indigo-blue with caustic soda and glucose, the subsequent operations being the same as those already described. An instantaneous reduction may be effected by treating the finely powdered indigo with a solution of a hyposulphite, obtained by agitating zinc-dust with a strong solution of acid sulphite of sodium, and treating the decanted liquid with excess of caustic soda.

[2] White indigo forms two compounds with lime, one of which is soluble and the other insoluble.

[3] A certain amount of indigotin is, however, never recovered; the cause of the loss is obscure, and its investigation would probably lead to means of preventing it which would well repay the trouble.

Concentrated sulphuric acid dissolves white indigo with intense purple coloration, forming mono- and di-indigotin-sulphonic acids.

INDIGOTIN-MONOSULPHONIC ACID. SULPHOPURPURIC ACID. Indigo-purpuric Acid. $C_{16}H_9N_2O_2.SO_3H$. This body, also called sulphophenicic acid, may be obtained by adding one part of good commercial indigo in fine powder to four parts of concentrated sulphuric acid, and heating the mixture for a short time, or until a sample gives a deep blue colour when largely diluted with water. Too high a temperature and too prolonged heating must be carefully avoided, or the disulphonic acid will be produced. As soon as the product is found to be soluble, the mass is thrown into about fifty parts of water, when a beautiful purple precipitate of sulphopurpuric acid will be thrown down. This is filtered off, and washed slightly with dilute hydrochloric acid.

Sulphopurpuric acid is almost insoluble in dilute acids and very sparingly soluble in water, but communicates a bluish-purple colour to the liquid. On adding sodium carbonate or acetate to the aqueous solution, purple flocks of the sodium sulphopurpurate, $C_{16}H_9N_2O_2.SO_3Na$, are precipitated. This salt is soluble in a large quantity of water, and is employed in dyeing under the name of *indigo-purple* or *red indigo-carmine*. Precipitates are produced by solutions of calcium, aluminium, and iron. Caustic alkalies produce no effect, but the solution is decolorised by reducing agents, such as zinc, sulphuretted hydrogen, or stannous chloride, and becomes blue again on exposure to the air.

INDIGOTIN-DISULPHONIC ACID. SULPHOINDIGOTIC ACID. $C_{16}H_8N_2O_2(SO_3H)_2$. This acid, also called indigo-sulphuric acid and sulphindylic acid, is obtained when the monosulphonic acid is heated with eight or ten parts of sulphuric acid, and hence is usually formed, to a greater or less extent, together with the monosulphonic acid, when indigo is treated with concentrated sulphuric acid. It forms the sole product when the sulphuric acid amounts to fifteen times the weight of the indigo employed. It is best obtained by carefully heating the finely pulverised commercial colouring matter, or preferably pure indigotin, with ten or twelve parts of ordinary strong sulphuric acid (sp. gr. 1·845), or six or seven parts of the fuming acid, to a temperature of 50° C. for several hours, or until a small sample is found to be entirely soluble in water. The product is then cooled and treated with about fifty parts of water. On standing for some time, any monosulphonic acid and certain other impurities will be deposited, and the filtered solution will be pure blue.[1] To prepare pure sulphindigotic acid, clean white wool or flannel, which has been previously thoroughly washed by boiling with soap and solution of carbonate of sodium and then with pure water, is immersed in the solution till the greater part of the colouring matter is taken up. It is then well washed to remove the free sulphuric acid, and stripped by immersing it in a weak solution of ammonium carbonate. The blue solution thus obtained is evaporated at a temperature not exceeding 50° C., and the residue treated with rectified spirit to dissolve any hyposulphindigotate. The undissolved portion, consisting of ammonium sulphindigotate, is treated with water, the solution precipitated by lead acetate, and the insoluble lead salt washed and decomposed by sulphuretted hydrogen. A colourless solution of hydrindigotin-disulphonic acid, $C_{16}H_{10}N_2O_2(SO_3H)_2$, results; and on exposure to air this readily oxidises to a blue solution of sulphindigotic acid, which may be obtained as a blue amorphous mass by evaporating the solution.

Sulphindigotic acid is decolorised by reducing agents. By oxidising agents it is converted into isatin-disulphonic acid, $C_{16}H_8N_2O_4(SO_3H)_2$, a body of an orange colour, on the formation of which several methods for the assay of commercial indigo are based.

Sulphindigotic acid is decomposed by an excess of strong caustic alkali, with production of a yellow liquid; but with dilute alkalies it reacts to form sulphindigotates. These salts, when solid, have a beautiful bronze-blue colour, and dissolve freely in pure water yielding blue solutions. In saline solutions they are almost or quite insoluble; and hence, on adding common salt or sulphate of sodium to the solution of a sulphindigotate of alkali-metal, the latter compound is precipitated in blue flakes.

Potassium sulphindigotate, $C_{16}H_8N_2O_2(SO_3K)_2$, is soluble in 140 parts of water, and the sodium salt somewhat more readily. The lead salt is insoluble, and the barium salt very slightly soluble in cold, but more readily in hot water. The sulphindigotates of calcium, magnesium, and aluminium are easily soluble.

INDIGO EXTRACT. SOLUBLE INDIGO. INDIGO-CARMINE. These names are applied in commerce to more or less pure indigo-sulphonic acids and their salts. The exact nature of the product varies considerably with the quality of the indigo, the proportion of sulphuric acid used, the temperature employed in the process, and the subsequent treatment of the sulphonated indigo.

---

[1] A third acid, called hyposulphindigotic acid, is said to be formed, but no formula has been assigned to it. In its reactions it closely resembles sulphindigotic acid, but its salts are soluble in rectified spirit.

With a moderate proportion of acid, the mono-sulphonic acid (page 298) is the chief product, and this, when converted into the sodium salt, is known as *indigo-purple* or *red indigo-carmine.* A product of similar composition, known as *Boiley's blue*, is prepared by gradually adding 1 part of finely powdered indigo to 10 or 20 parts of sodium hydrogen sulphate, $NaHSO_4$, in a state of fusion. The product is dissolved in water, precipitated with common salt, and washed with brine. Boiley's blue is a crystalline, light purplish mass, soluble in water with beautiful blue-violet colour. Its solution in strong boiling acetic acid deposits, on cooling, large prismatic crystals, exhibiting a coppery reflection. It is insoluble in alcohol or ether, but readily soluble in hot water. The light transmitted by the solution is red. With barium and strontium salts it yields violet precipitates.

Saxony blue, chemic, chemic blue, and *sour extract* are names applied to the solution of indigo in sulphuric acid, without any neutralisation or subsequent treatment. It is not unsuitable for wool-dyeing, as the green colouring matter which it generally contains has no affinity for the wool-fibre; but for dyeing silk this must be removed. For this purpose the acid is usually converted into a sodium salt, known as *indigo-carmine.* This can be made by neutralising the acid with soda-crystals, when the sodium sulphate simultaneously formed precipitates the sodium sulphindigotate, the separation being rendered complete by adding common salt. The precipitate may be purified by re-solution in water, and again salting out, the process being repeated until the absence of a green tint in the filtered liquid shows that the objectionable green colouring matter has been entirely removed. The purified precipitate should then be washed with water until the liquid begins to run through blue, when it is drained and pressed. In some cases the solution of the sulphonated indigo is at once precipitated with common salt, without being previously neutralised. Magnesia and chalk are sometimes employed instead of soda-crystals. The potassium salt, obtained by precipitating a solution of sulphindigotic acid by potassium acetate, is occasionally met with.

Indigo-carmine occurs in commerce as a dry powder or copper-coloured masses having a blue streak, and also as a blue or purple paste, which should be free from any green or brown reflection. The following figures (page 301) indicate the usual percentage composition of indigo pastes.

The *water* is determined by drying 2 grammes of the sample at 100°, and noting the loss of weight. The dried substance is then heated just to redness in platinum, when the residue represents the *saline matters*, the loss being regarded as *organic matter.* The figure thus obtained is sometimes reported as "colouring matter," but in reality is made up of water not driven off at 100°, sulphuric acid evolved from $NaHSO_4$, organic impurities of the indigo, &c. As the real colouring matter of indigo-carmine usually ranges from 2 to 5 per cent., with an average of about 3 per cent., it is evident that the organic matter of a sample does not, even approximately, indicate its tinctorial value. The indication is still more worthless in presence of *dextrin* and other adulterants. A useful method of assaying indigo-carmine is to dissolve 1 gramme of the sample in a litre of water, and compare the depth of colour with that yielded by a standard specimen; but the difference in the shade of various makes of indigo-paste often renders this method of examination untrustworthy. In such cases the true strength of the sample is best ascertained by titration with permanganate or hyposulphite, as described on pages 308, 309.

	Organic Matter.	Saline Matters.	Water.
Best quality	12·4	13·9	78·7
Second quality [1]	10·2	4·8	85·0
Third quality	4·96	5·70	89·34
No. 1	10·8	4·7	84·5
No. 2 [2]	5·6	4·7	89·7
No. 3	9·55	7·80	82·65

The presence of the green colouring matter in indigo-paste may be detected by rubbing a little of the colouring matter on glazed paper. On drying, the shade will vary from pale blue to a rich coppery-purple, according to the mode of manufacturing the paste; and if any green colouring matter be present, a green border will be observed surrounding the blue circle. The test may be modified by dropping an aqueous solution of the colouring matter on a piece of filter-paper, when the green margin will become evident as the paper dries.

Indigo-extracts should leave no undissolved gritty particles when treated with water, but all the common varieties leave a dirty greenish-black insoluble residue. Soluble indigo is said to be sometimes adulterated with farina, dextrin, and other inert matters. A general indication of the quality of the sample may be obtained by dissolving a known weight in water, adding a little alum and cream of tartar, and then introducing successive swatches of well-washed white wool or flannel. The value of the sample will be in proportion to the weight of wool dyed to a standard shade of colour. The green colouring matter already referred to as occurring in some qualities of soluble indigo is taken up by wool last, or not at all, when the sample is thus treated.

---

[1] From F. Crace-Calvert's valuable work on *Dyeing and Calico Printing*.

[2] From *Färb. Must. Zeit.*, 17, 131; abstracted in *Jour. Soc. Chem. Ind.*, ii. 374.

The more acid varieties of soluble indigo are employed for dyeing wool and worsted. The neutral is employed for silk, and is also used for dyeing mixed goods, containing cotton, and for printing woollen goods, such as tapestry-carpets, &c. The dyeing is effected in an acid bath, to which cream of tartar, sodium sulphate, or alum is sometimes added.

COMMERCIAL INDIGO.—Indigo occurs in commerce in lumps or fragments of a deep blue colour, usually showing a bronze or purple-red streak when rubbed with any hard substance, or, in the case of the better kinds, even with the friction of the thumb only. The fracture of indigo is dull and earthy, and it is practically insoluble in water or any of the ordinary solvents, except concentrated sulphuric acid.

Indigo varies much in quality according to the care taken in its preparation.[1] The indigotin or indigo-blue, which is the most valuable and abundant constituent, varies from 20 to (occasionally) 80 per cent., with an average of about 45 per cent. The only other constituent of tinctorial value is the indirubin or indigo-red, the proportion of which is generally between 3 and 5 per cent. Chlorophyll (more or less altered), a brown colouring matter called indigo-brown, and a gluten-like substance termed indigo-gluten, are the other principal constituents, in addition to a trifling percentage of moisture and a variable proportion of mineral matter.

When an indigo of superior quality is required, as is desirable for making indigo-extract, the finely powdered substance is treated several times at a gentle heat with hydrochloric acid containing a little free chlorine, by which treatment iron, lime, and some other mineral impurities are dissolved, while the amylaceous matters are converted into dextrin or sugar, which is removed by subsequent washing with water. The residue is then treated with weak caustic soda, which removes chlorophyll and some other organic impurities. The product is known in commerce as *refined indigo*. The same name is applied commercially to a product obtained by reducing finely-ground indigo with ferrous sulphate and lime.

The technical analysis of indigo is usually limited to determinations of the moisture, ash, specific gravity, and colouring matter. In some cases the indigotin is the only colouring matter taken into account, but the indirubin ought not to be neglected, as it modifies the shade of the blue produced, and is itself capable of dyeing any fast colours. Indigo-brown, on the other hand, is of no practical interest, as in the dye-vat it forms an insoluble compound with the lime used, and in making extract is precipitated when the sulphuric acid solution of the indigo is diluted with water. The methods of determining the proportion of colouring matter in indigo are very numerous, but few can be at once considered both accurate and practical.[1]

---

[1] See a paper on West African Indigo by Rawson and Knecht, in the *Jour. Soc. Dyers, &c.*, iv. 66.

The *moisture* in commercial indigo usually ranges from 3 to 8 per cent., and may be determined with accuracy by observing the loss of weight undergone by the sample on exposure to the temperature of boiling water.

The *ash* left on igniting commercial indigo is a useful criterion of its purity. In the purest kinds it is sometimes as low as 2 per cent., but from 5 to 8 per cent. is a more usual proportion. Some of the inferior kinds of indigo, such as Kurpah and Madras, frequently contain from 25 to 35 per cent. of ash.

Leuches has recommended the determination of the *specific gravity* as a useful preliminary test of the quality of indigo, and gives the following figures in illustration of the relation between the specific gravity and percentage of indigotin :—

Specific gravity,	1·324	1·332	1·350	1·371	1·384	1·421	1·437	1·455
Indigotin, per cent.	56	55	53	49	44	40	37	35

Helen Cooley (*Amer. Jour. Anal. Chem.*, ii. 130) has recorded the specific gravities and percentages of ash and indigotin contained in the following samples of commercial indigo :—

Description.	Specific gravity.	Ash.	Indigotin.
Kurpah blue, . .	1·129	17·54	55·11
Watson's best, . .	1·292	6·50	59·53
Bengal red, . . .	1·391	6·41	54·03
Oude, ...	1·427	7·02	52·90
Bengal blue, . .	1·431	7·50	57·60
Kurpah red, . .	1·529	21·20	45·28
Guatemala, . . .	1·559	14·49	47·04

These figures do not establish the value of the specific gravity as a test of quality, or even indicate that it is a criterion of the proportion of ash.

---

[1] The valuation of indigo has been treated in an exhaustive manner by C. Rawson (*Jour. Soc. Dyers, &c.*, i. 74, 211), from whose paper much of the information here given is derived, and to whom the author is indebted for the perusal and correction of this article on the subject.

Starch, sometimes coloured with iodine, is said to be occasionally employed for adulterating indigo. To detect it, the sample should be treated with a cold dilute solution of sodium thiosulphate, and the insoluble residue washed with proof spirit. The starch-granules may then be detected by the microscope, or the residue may be boiled with water and the starch tested for by adding iodine solution to the filtered liquid.

A useful *proximate analysis* of indigo, together with a moderately accurate determination of the indigotin present, may be effected as follows:—The sample is dried at 100° to determine the water, then treated with hot water and the residue dried and weighed. This gives the matters soluble in water, and the residue is treated in succession with dilute hydrochloric acid, dilute caustic soda, and alcohol. The loss of weight resulting from each of these treatments may be determined with advantage, especially the amount of matter soluble in alcohol, as this represents the *indigo-red* of the sample.[1] The residue after this treatment is dried and weighed. Its weight, after deducting that of any ash it may leave on ignition, represents the *indigotin* of the sample.

C. Tennant Lee (*Chem. News*, l. 49; from *Jour. American Chem. Soc.*) has proposed to assay indigo by observing the amount of indigotin which can be obtained by sublimation—a method which is easy, rapid, and, in his experience, uniformly satisfactory. For the operation he recommends the use of a shallow, flat-bottomed, platinum tray, 7 centimetres in length, 2 wide, and 0·3 or 0·4 deep. About 0·25 gramme of the finely powdered sample, previously dried at 100°, is introduced and spread evenly over the bottom of the tray, which is then gradually heated on an iron plate. When the surface of the indigo becomes covered with a shining layer of crystals, the tray is covered with a piece of sheet iron, about 8 or 9 centimetres in length and bent into a slightly arched form, so that the highest point may be about 1 cm. above the plate. The heat is simultaneously lowered. Purple vapours of indigotin are now given off, a portion condensing on the concave side of the arch. The heat is now raised slowly, so as to maintain a constant sublimation of indigotin, the progress of which can be observed by raising the arch. With a 50 per cent. indigo, the operation is complete in 30 to 40 minutes; but soft Java indigo must be treated with more caution, the sublimation sometimes occupying two hours. When all crystals of indigotin have disappeared from the dark-coloured surface of the residue, the tray is removed, cooled in a desiccator, and weighed, the loss of weight being regarded as *indigotin.* On repeating the process the results should not vary more than 0·3 per cent. C. Rawson points out that the author of the above process has not given any figures by which the results obtained can be compared with those yielded by other methods. In his own experience he has found the agreement to be in many cases very good; but, as a rule, inferior qualities of indigo, containing much matter soluble in hydrochloric acid, yield by the sublimation-process results above the truth; whilst, on the other hand, rich samples give results which are undoubtedly too low. Rawson obtained differences of upwards of 2 per cent. by an alteration in the cover. It seems probable that these strictures are justified, but that the process is nevertheless very useful in many cases. If applied to indigo which had been subjected to a preliminary treatment with dilute hydrochloric acid, and then thoroughly dried, it would probably yield, on subjection to carefully-regulated sublimation, results of considerable accuracy.

---

[1] As indigo-brown is only with difficulty removed by treating indigo with caustic soda, the indigo-red is liable to be contaminated with the portion of the brown which escaped solution. By treating the impure product with dilute caustic alkali, the indigo-brown will be readily dissolved and the indirubin obtained pure.

Another method of estimating the real indigotin present in commercial indigo is based on its reduction to the leuco-derivative (white indigo), and reoxidation of this by exposure to air. Some of the processes for effecting this are tedious and deficient in accuracy, but the following, in one of which the reduction is effected by a ferrous hydroxide and in the other by a hyposulphite, are recommended by C. Rawson. The iron process is conducted by treating 1 gramme of the finely powdered sample in a flask with 2 grammes of crystallised ferrous sulphate, 5 of caustic soda, and 1000 c.c. of water. The flask is closed by a cork having three perforations, through one of which passes a syphon, while the other two are used for the entrance and exit of a current of coal-gas. The contents of the flask are maintained at a temperature a little below the boiling point for 1½ to 2 hours, when the source of heat is removed and the insoluble matters allowed to subside. A measure of 500 c.c. (= ½ gramme of the sample) is now syphoned off, and the reduced indigo oxidised by passing a current of air through the solution. To complete the precipitation, the liquid is acidified, and the precipitate of indigotin, mixed with indirubin and indigo-brown, allowed to subside. The supernatant liquid is passed through a weighed filter, and the precipitation washed several times by decantation with hot water. It is then boiled with alcohol, which dissolves the brown and red colouring matters, allowed to cool to insure the separation of any traces of dissolved indigotin, transferred to the filter, washed with rectified spirit, and the pure indigotin dried at 100° and weighed.

The following method is preferred by C. Rawson, as leaving nothing to be desired in point of accuracy, and being more rapid than any other reduction-process:—1 gramme of the finely powdered sample is made into a paste with water, and treated in a flask with about 600 c.c. of lime-water. The flask is closed by a cork having four perforations, two of which serve for the passage of a current of coal-gas, a third carries a syphon, while to the fourth is fitted a tap-funnel. The contents of the flask are heated to 80° C., and 100 to 150 c.c. of a strong solution of sodium hyposulphite ($NaHSO_2$) introduced through the tap-funnel.[1] In a few minutes the liquid assumes a yellow tint, and is maintained at a temperature near the boiling point for half an hour. After allowing the insoluble matters to subside, an aliquot part of the solution should be removed and a current of air drawn through it for about twenty minutes, when it is acidulated with hydrochloric acid. The precipitate, consisting of a mixture of indigotin and indirubin, is collected on a weighed filter, thoroughly washed with hot water, dried at 100°, and weighed. It is then exhausted by boiling alcohol, whereby the indirubin is dissolved, and can be estimated from the loss of weight or recovered by evaporating the alcoholic solution.

Although, with care, the precipitate of mixed indigotin and indirubin obtained as above may usually be obtained free from impurities, in some cases Rawson recommends that the dried precipitate should be dissolved in pure concentrated sulphuric acid at 85° C., and an aliquot part of the diluted solution titrated with $\frac{N}{50}$ permanganate, each 1 c.c. of which, according to him, corresponds to 0·0015 gramme of indigotin.

In a method described by H. M. Rau (*Jour. Amer. Chem. Soc.*, 1885, 7, 16), which is a modification of one previously suggested by Fritsche (*Annal. Chem.*, xliv. 290), the indigo is reduced in alkaline solution by glucose. The operation is conducted in a weighed flask of about 8 oz. capacity, fitted with a cork carrying two tubes. From 1½ to 2 grammes of the sample of indigo, 3 to 4 of pure grape sugar, from 5 to 10 c.c. of a 40 per cent. solution of caustic soda, 60 c.c. of water, and about 120 c.c. of rectified spirit are employed, and the total weight of the apparatus is observed. The flask is heated in a water-bath for half an hour, and allowed rest for another hour. One of the two tubes is then connected with an apparatus generating carbon dioxide, by which the liquid is blown out through the other tube, which is arranged as a syphon, and the shorter limb of which is loosely plugged with glass-wool. The weight of the liquid expelled is noted, and the indigotin is then precipitated by passing a current of carbon dioxide for about fifteen minutes, and this is followed by a current of air to complete the precipitation. The precipitate is crystalline, and is readily washed. It is stated by Rau to represent the indigotin and indirubin of the sample, but Rawson has pointed out (*Jour. Soc. Dyers, &c.*, i. 211) that the solubility of indirubin in alcohol renders its precipitation improbable, and he has proved by actual experiment that the precipitate obtained by Rau's process consists of pure *indigotin*, yielding nothing either to cold alcohol nor to ether.

---

[1] The sodium hyposulphite, which must not be confounded with the thiosulphite, $Na_2S_2O_3$, is prepared by treating a solution of sodium hydrogen sulphite ($NaHSO_3$) with zinc-dust in a closed flask. After standing about one hour, with occasional agitation, the liquid is decanted and diluted with a litre of recently boiled distilled water. About 50 grammes of slaked lime should be next added, the vessel closed, and when the precipitate has subsided the clear liquid is syphoned off and kept under a layer of kerosene oil, in a bottle protected from the light.

A volumetric method of determining indigotin has been described by L. M. Norton (*Amer. Assoc. Adv. Science*, 1880, p. 358). One gramme of the sample is mixed in a mortar with milk of lime, and the paste washed into a flask. One gramme of zinc-dust is added, and water added to a mark on the neck. The flask is then heated on the water-bath for half an hour, closed, and allowed to stand overnight. In the morning the contents are shaken, allowed to settle, and a volume of 100 c.c. blown out by a neutral gas into a solution of iron-alum. The ferrous salt formed corresponds to the reduced indigo in the volume taken, and is determined by titration with a standard solution of bichromate. Helen Cooley (*Amer. Jour. Anal. Chem.*, ii. 133) states that the manipulation is simple, and that, with some practice, the method gives good results.

A variety of methods of assaying indigo have been based on the oxidation of the colouring matter in acid solution. Thus, potassium permanganate, bichromate, and ferricyanide have all been recommended and used to a considerable extent, and bleaching powder solution has also been employed. All these processes are open to the objection that the oxidising agent acts on the indigo-gluten and ferrous salts, as well as on the indigo-red and indigo-blue, and hence the results are liable to be seriously above the truth; but Rawson has pointed out that the errors due to this cause may be practically avoided by previously precipitating the sulphindigotic acid in the form of the sodium salt, by adding common salt to the solution. He recommends the following method of working:—1 gramme of the sample of indigo in the form of impalpable powder is mixed in a small mortar with about its own weight of ground glass. This mixture is gradually and carefully added, during constant stirring with a glass rod, to 20 c.c. of concentrated sulphuric acid (sp. gr. 1·845), which is then heated to about 85° C. for an hour.[1] The product is then cooled, diluted with water to 1 litre, and filtered from indigo-brown and other insoluble matters. If the solution be now at once titrated with permanganate the results are liable to be seriously above the truth, owing to the presence of sulphurous acid, ferrous salts, indigo-gluten or the products of its decomposition, and other oxidisable matters. To eliminate this source of error, Rawson recommends that 50 c.c. of the filtered solution should be treated with 50 c.c. of water and 32 grammes of common salt, which quantity is almost sufficient to saturate the liquid. After standing for two hours,[2] the solution is filtered and the precipitate washed with about 50 c.c. of brine of 1·2 sp. gr. The precipitated sodium sulphindigotate is dissolved in hot water, and the solution cooled, mixed with 1 c.c. of sulphuric acid, and diluted to 300 c.c. This solution is then titrated in a porcelain dish with a solution of potassium permanganate, containing 0·5 gramme of the solid salt per litre,[3] the exact oxidising power of which has been ascertained by experiment with a solution of pure indigotin. This is made by dissolving 0·5 gramme in strong sulphuric acid, diluting the solution to 1 litre, and employing 50 c.c. of the solution and 250 c.c. of water for the titration. The oxidation is regarded as complete when the liquid, which first takes a greenish tint, changes to a light yellow, with a faint pink colour on the margin (compare page 110). A correction should be made for the small quantity of sodium sulphindigotate which escapes precipitation by the salt, and which Rawson finds to be equivalent to 1 milligramme of indigotin.

Instead of precipitating the sodium sulphindigotate by salt, as recommended by Rawson, it is in many cases sufficient to mix the sample of indigo with powdered glass, and treat with hot hydrochloric acid of moderate strength, filtering, washing the insoluble portion with water, drying, and treating with sulphuric acid.[1] Whether or not this treatment be substituted for precipitation of the sulphindigotate, it is essential, in order to obtain accurate results, that the dilute solution in sulphuric acid should be *filtered*, to remove indigo-brown and other organic matters having a reducing action on the permanganate.

---

[1] The temperature and time recommended in the test should not be greatly exceeded. The sulphuric acid employed for dissolving the indigo must be free from arsenic and nitrous compounds. The first condition may be ensured by well-known means, the second by heating the acid with a few crystals of ammonium sulphate.

[2] Rawson states that if the liquid be strongly agitated, by drawing a current of air through the solution, the precipitate completely separates in less than half an hour.

[3] Instead of permanganate of this strength, $\frac{N}{50}$ solution (0·6324 gramme per litre of $KMnO_4$) may be used. According to Rawson, 1 c.c. of this oxidises 0·0015 gramme of indigotin.

Other oxidising agents, such as potassium ferricyanide or bichromate, which have been recommended for titrating the solution of sulphindigotate, present no advantage over permanganate, and the end-reaction is not so well defined.

Instead of assaying the solution of sulphindigotic acid or its sodium salt by an oxidising agent, a suitable reducing agent may be substituted. **Mulder** has proposed the use of stannous chloride for the purpose, and **Bernthsen** and **Drews** (*Chem. News*, xliii. 80) have suggested Schützenberger's hyposulphite of sodium ($NaHSO_2$) for reducing sulphindigotic acid. They find the reduction to occur in a strictly quantitative manner, according to the equation :—

$$C_{16}H_8N_2O_2(SO_3H)_2 + NaHSO_2 + H_2O = C_{16}H_{10}N_2O_2(SO_3H)_2 + NaHSO_3.$$

A. **Müller** has also recommended the utilisation of this reaction, and C. **Rawson** considers that, of all the volumetric methods which have been devised for estimating "indigotin," the hyposulphite process is capable of giving the most rapid and accurate results, but considerable care and delicacy are required in the manipulation.

If iron be present in the ferric state, the results obtained by the hyposulphite process will be above the truth, but it is only in the lower classes of indigo that this impurity is present, and in those cases it principally exists in, or becomes subsequently reduced to, the ferrous state. Of course, treatment of the sample with hydrochloric acid, or precipitation of the sulphindigotate by salt, can be resorted to if requisite. Neither indigo-gluten, indigo-brown, nor indigo-red has any appreciable oxidising action on sodium hyposulphite. Hence the method is one which effects a determination of *actual indigotin* present, and is in that respect less adapted for the commercial valuation of indigo than a method like that of oxidation by permanganate, which also takes cognisance of the indirubin of the sample.

---

[1] If the treatment with salt be omitted, the solution of the indigo in sulphuric acid should be somewhat diluted, boiled for fifteen minutes to drive off sulphurous acid, cooled, and diluted to 1 litre.

The use of sodium hyposulphite for reducing indigo in presence of an alkali has already been described. Its application to acid solutions of indigo and to the assay of indigo-carmine is carried out by Rawson as follows:—A standard solution of cupric sulphate is prepared by dissolving 1·904 gramme of the crystallised salt ($CuSO_4,5H_2O$) in water, adding 100 c.c. of strong ammonia (sp. gr. 0·880), and diluting to 1 litre. 50 c.c. of this solution is boiled in a wide-mouthed flask of about 200 c.c. capacity, to expel air, and allowed to cool. The flask is fitted with a caoutchouc stopper pierced with four holes, two of which serve for the entrance and egress of a current of coal-gas, while into the other two are fitted the noses of two Mohr's burettes containing the solutions of sodium sulphindigotate and sodium hyposulphite respectively. The latter solution should be of one-fifth of the strength of that employed for the alkaline reduction-process (page 306), and the burette containing it is attached to the stock-bottle of standard solution in such a manner that it can be refilled without introducing air. A current of coal-gas (previously caused to traverse a V-tube, charged with a mixture of milk of lime and solution of ferrous sulphate) is passed through the flask containing the measured quantity of copper solution, and the solution of sodium hyposulphite is then gradually run in until the liquid becomes nearly colourless, when a few drops of indigo-carmine solution are added from the other burette, and finally a further quantity of hyposulphite is added until the solution assumes a peculiar brownish-red colour. The volume of hyposulphite employed, after making a slight correction for that requisite to reduce the sulphindigotate, represents the quantity required to reduce ·050 gramme of indigotin, this being the amount to which 50 c.c. of the standard copper solution is equivalent. The strength of the hyposulphite solution having been thus ascertained, a measure of 50 c.c. of sulphindigotic acid solution, prepared as already described, is introduced into the flask, boiled to expel air, and allowed to cool. The flask is then attached to the burettes, coal-gas passed as before, and the hyposulphite solution gradually added during constant agitation. With pure indigotin and the better qualities of indigo, the liquid, when fully reduced, becomes of a pale yellow tint, but in the case of inferior samples it has a more or less dirty brownish-yellow colour. In both cases, however, the end of the reaction is perfectly well defined.

C. Rawson (*Jour. Soc. Dyers, &c.*, i. 79) gives the following figures showing the results yielded by six typical samples of commercial indigo when examined by the principal of the methods already described. The figures (all of which are the means of several determinations) are valuable as showing the influence of the presence of impurities on the results obtained :—

	Java.	Bengal.	Bengal.	Oude.	Kurpah.	Madras.
Water.	2·99	5·22	6·17	7·50	8·05	5·71
Ash.	1·99	3·91	4·86	8·21	25·72	33·62
Indigotin ; by sublimation.	60·84	57·50	49·36	41·60	41·92	39·56
Indigotin ; volumetric, by hyposulphite.	68·78	59·26	55·66	43·18	42·52	36·30
Indigotin; gravimetric, by $FeSO_4$ and NaHO.	68·24	58·84	54·34	44·50	41·50	34·50
Indigotin ; gravimetric, by hyposulphite and lime.	68·97	59·12	56·20	43·42	42·68	35·21
Indirubin ; separated by alcohol.	4·23	3·50	2·80	3·65	2·45	3·98
Indigotin and indirubin ; titration with $KMnO_4$ direct.	76·18	66·71	62·66	50·04	47·15	39·50
Indigotin and indirubin ; after precipitation with salt.	73·55	63·50	57·50	44·90	43·10	37·40

Helen Cooley (*Amer. Jour. Anal. Chem.*, ii. 137) gives the following figures (among others) in illustration of the results yielded by different processes of assaying indigo (compare page 303).

	Kurpah.		Bengal.		Oude.	Guatemala.
	Red.	Blue.	Red.	Blue.		
Indigotin ; by sublimation.	45·40	56·84	55·99	57·54	52·58	47·08
Indigotin ; gravimetric, by NaHO and glucose.	45·28	55·21	53·79	57·06	57·72	47·10
Indigotin ; volumetric, Norton's process.	45·48	55·23	53·13	57·27	51·53	47·14
Indigotin and indirubin ; precipitation with salt and titration with $KMnO_4$.	...	...	64·10	60·89	51·88	...

In criticising these results (*Amer. Jour. Anal. Chem.*, ii. 368), C. Rawson points out that higher figures are to be expected by a process which takes cognisance of the presence of indirubin than by one which is unaffected by this constituent of indigo, and he attributes the higher results obtained by the permanganate process at least in part to this cause, though over-heating with sulphuric acid may also have contributed to the result. In a sample of African indigo he has met with 8 per cent. of indirubin and 32 of indigotin.

The assay of indigo by dyeing swatches of cloth under specified conditions is useful in some cases, but the results cannot be compared in accuracy or delicacy with those obtained by chemical methods; and on assaying a series of samples a repetition of the test will very frequently fail to show the same gradation between them. The method of operating is to mix 2 grammes of the sample of indigo and 1 gramme of lime into a paste with water, transfer the mixture to a large beaker, add 1 gramme of zinc-dust, and make up the volume to 600 c.c. The whole is then heated on the water-bath for an hour, and a piece of white calico or swatch of cotton yarn of known weight introduced. It is then removed, squeezed, and exposed to the air till the blue colour is fully developed, when it is compared with similar pieces of cotton which have been dyed by pure indigotin, or standard indigo, in precisely the same manner.

A preferable method to the above is to treat 0·5 gramme of the sample with 6 grammes of strong sulphuric acid at 85° C. for an hour, and dilute the solution to 1000 c.c. 10 c.c. of this solution is then further diluted with a known quantity of water, and used for dyeing 5 grammes of white wool. About ·05 gramme of sodium sulphate and a drop or two of sulphuric acid may be advantageously added to the bath before immersing the wool.

A colorimetric test, based on the depth of tint of the sulphindigotic solution, can be made under favourable conditions, but is valueless for comparing samples of indigo containing variable proportions of indigo-red and other secondary colouring matters, owing to the different shade which the solution possesses in such cases. C. H. Wolff (*Jour. Soc. Chem. Ind.*, iii. 516) has proposed to avoid this difficulty by observing the absorption-spectrum of the solution (1 in 800,000). H. Cooley states that the method gives fair results with indigoes of high quality, but is useless for the lower grades.

Detection of Indigo on the Fibre. The colouring-matter deposited in the fibre when a fabric has been dyed in the indigo-vat consists essentially of indigotin, but when soluble indigo has been employed the dye is taken up in the form of mono- or di-indigotin-sulphonic acid.

Fibres dyed in the indigo-vat are unaffected by hydrochloric acid, dilute sulphuric acid, soda, or ammonia. On heating with an acid solution of stannous chloride the fibre becomes paler, and a greenish-yellow solution is formed. Concentrated sulphuric acid gives a blue solution, and boiling absolute alcohol also dissolves the dye with blue colour, the solution becoming colourless on standing, with separation of indigotin. Chloroform, amylic alcohol, glacial acetic acid, phenol, and aniline also give blue solutions when heated with indigo-dyed fibres.[1] On carefully heating a fabric which has been dyed in the indigo-vat, it gives off purple vapours, which can be condensed on the cover of a porcelain crucible to a blue spot.

Indigo is now frequently used in admixture with other colouring matters, some of which are difficult to recognise in presence of indigo. W. Lenz (*Jour. Soc. Dyers, &c.*, iii. 127, 140, 150, 178) states that woollen goods (*e.g.*, yarn) which have been dyed with vat-indigo only must satisfy the following conditions:—Water, even when hot, should not extract any colouring matter; alcohol, of 50 and 95 per cent. strength by volume, should not, as a rule, extract any colouring matter on *gently* warming; oxalic acid solution saturated cold, cold saturated borax solution, 10 per cent. alum solution, and solution of ammonium molybdate in two parts of water should none of them, when used boiling, extract any colouring matter from the fibre; and the borax solution should not be coloured red by hydrochloric acid (campeachy), or give a blue coloration or precipitate on subsequently adding ferric chloride (prussian blue). On the other hand, the blue colour should be completely destroyed on warming the fibre with an acid solution of stannous chloride or ferric chloride. Glacial acetic acid should entirely remove the colour after repeated treatment, and on treating the solution obtained with twice its measure of ether, and adding water in sufficient quantity to cause the ether to separate, the ethereal layer should appear distinctly, but not very intensely, blue, while a deposit of indigotin should appear at the junction of the two layers. The lower layer should be colourless, and remain so when a little concentrated hydrochloric acid is poured into it through the ether. On boiling the fibre with concentrated hydrochloric acid, no sulphuretted hydrogen should be evolved; and after continued boiling, till the fibres are decomposed, treatment of the solution with strong caustic soda in large excess, warming, and adding a few drops of chloroform, no odour of isonitril should be observable (aniline blues).

Fibres which have been dyed with sulphonated indigo (indigo-carmine, soluble indigo) give a greenish-blue solution when treated with hydrochloric acid, and strong sulphuric acid yields a blue solution. Little or no colour is removed by alcohol. Caustic soda turns the fibre greenish, and on boiling with the dilute alkali the dye is removed without the solution becoming much coloured, until it is acidulated, when it becomes blue. Ammonia behaves similarly. The colour is also removed by boiling with dilute sodium carbonate, and silk or wool may be dyed blue in the acidulated solution. Heated with an acid solution of stannous chloride, the fibre is decolorised. With nitric acid, goods dyed with sulphonated indigo behave like those dyed in the indigo-vat. When boiled with a solution of borax (saturated in the cold), goods dyed with indigo-carmine are decolorised, while if dyed with vat-indigo the colour is not affected. Indigo-carmine colours the borax solution blue, and the liquid is decolorised when warmed with stannous chloride and hydrochloric acid. Glacial acetic acid does not remove the colour from fibres dyed with indigo-carmine.

---

[1] Strong nitric acid gives a yellow spot on indigo-dyed goods. This reaction is employed as a rough practical test for the quality of indigo-dyed goods. The cloth is first spotted with hydrochloric acid, which will produce no change with indigo, but will change logwood dyes to red. The fabric is then spotted with nitric acid, which, if the cloth be of good quality and indigo-dyed, will produce a yellowish-red stain, surrounded by a bluish-green ring. An inferior sample gives a red stain and no definite ring.

The determination of the amount of indigotin fixed on fibres is sometimes of interest, since, as a rule, neither the quantity of indigo contained in the vat nor the exact quality of the indigo used is known. The determination may be effected by completely extracting the fibre with glacial acetic acid, precipitating the indigotin from the resultant solution by addition of water, and either at once collecting and weighing it or determining it by one of the processes used for the assay of commercial indigo. In some cases it is desirable to remove other colouring matters from the fibre by treatment first with cold hydrochloric acid, and then with a boiling solution of oxalic acid saturated in the cold. Sulphonated indigo is not stripped by glacial acetic acid, but may be removed from the fibre by boiling with borax solution in the manner already described.

A. Renard (*Jour. Soc. Dyers, &c.*, iii. 4) determines the indigo on fabrics by a direct application of sodium hyposulphite and lime to the fibre. He treats 10 grammes of the fibre with 200 c.c. of a solution prepared by adding 2 litres of water and 100 c.c. of milk of lime to 100 c.c. of neutral sodium hyposulphite prepared from bisulphite solution of 1·32 sp. gravity. The liquid is heated to 60° or 70° C. till the fibres are decolorised, when a current of coal-gas is passed through the flask employed and the contents shaken till every trace of blue has disappeared, when the liquid is decanted into a graduated cylinder without interrupting the current of gas. After cooling, the exact volume of the decanted liquid is observed, excess of hydrochloric acid added, and the precipitated indigotin filtered off after twelve hours, washed, dried, and dissolved in sulphuric acid, the resultant solution being subsequently titrated with standard hyposulphite, as described on p. 310. Renard found the amount of indigotin fixed on cotton fibre to range from 1 to 3 per cent. The method is applicable in presence of aniline blues, and with an obvious modification would serve for the assay of fabrics dyed with sulphonated indigo.

Colouring Matters from Lichens.

Several kinds of lichens acquire a violet colour under the joint influence of ammonia and atmospheric oxygen. This fact depends on the presence of one or two peculiar principles, and was known and practically utilised long before it received a satisfactory explanation.

The colouring matters of industrial importance obtained from lichens are three in number, namely:—*Archil*, *orseille*, or *orchil*; *cudbear*, known on the Continent as *perseo*; and *litmus* or *tournesol*. The two principal species of lichen which yield archil are *Rocella fuciformis*, which furnishes the products from Lima, Angola, Zanzibar, Ceylon, and Mozambique; and *Rocella tinctoria*, growing in Cape Verde and the neighbouring islands, Chili, &c. The first species contains a peculiar principle called erythrin, convertible into a red dye by the united action of air and ammonia; while the latter contains, in addition, a chromogen called lecanoric or orcellic acid and its homologue evernic acid. Cudbear is obtained from the Swedish lichen, *Lecanoria tartarea*.

The value of the various lichens or "archil weeds," from which archil and the allied colouring matters are prepared, depends on the proportion of orcin obtainable from them. This may be ascertained approximately by the following volumetric process devised by Stenhouse:—10 grammes weight of the finely divided lichen is macerated three or four times in succession with a dilute solution (5 per cent.) of caustic soda, each treatment being only extended to a few minutes' duration. The strained or filtered solutions are then mixed and titrated with a standard solution of sodium hypochlorite, which must be gradually added. Each drop of the hypochlorite produces a blood-red coloration, which changes to yellow in the course of a few seconds. The addition is continued cautiously as long as this reaction is produced. The hypochlorite solution must be freshly prepared, and its strength ascertained by titration with pure orcin or a lichen of known quality.

S. Reymann has proposed to assay archil weeds for orcin by acidulating the solution obtained by macerating the lichens with caustic soda and titrating the solution with a hypobromite (see page 319).

Erythrin or Erythric Acid, $C_{20}H_{22}O_{10}$, may be prepared from *Rocella fuciformis* by macerating the lichen in the cold with milk of lime. The filtered liquid is acidulated with hydrochloric acid, when the erythrin is precipitated as a hydrate of the formula $2C_{20}H_{22}O_{10}+3H_2O$, which is filtered off and washed. It becomes anhydrous at 100° and melts at 137° C. Erythrin is nearly insoluble in cold water, but dissolves in 240 parts of boiling water, and is deposited from the hot solution on cooling as a colourless crystalline powder, only slightly soluble in cold alcohol or ether, but more soluble in hot alcohol, from which solvent it crystallises in stellate groups of needles. The solution gives a white precipitate with basic lead acetate, but none with the neutral acetate. With ferric chloride it gives a fine purple or violet coloration, changing to a brownish-red precipitate with excess of the reagent. Erythrin exhibits the characters of a weak acid, dissolving in solutions of caustic and carbonated alkalies and of the alkaline earths, from which solutions it is thrown down as a bulky white precipitate on addition of an acid. The ammoniacal solution of erythrin becomes red on exposure to the air.

If the solution of erythrin in alkali be boiled, decomposition ensues, the erythrin splitting up into picro-erythrin, $C_{12}H_{16}O_7$, and orcellinic acid, $C_8H_8O_4$, while on further treatment the picroerythrin is decomposed into orcinol, $C_7H_8O_2$, erythrol, $C_4H_{10}O_4$, and carbon dioxide. These reactions establish the constitution of erythrin as the di-orcinillic ether of erythrol, and that of picroerythrin as the mono-orcellinate of the same alcohol. The relationship of these and allied bodies is shown by the following formulæ:[1]—

Orcinol, ...	$C_6H_2(CH_3)(OH)_2.H$
Orcellinic acid, . . .	$C_6H_2(CH_3)(OH)_2.CO.OH$
Diorcellinic acid, . .	$\left\{\begin{array}{l} O.C_6H_2(CH_3)(OH).CO.OH \\ CO.C_6H_2(CH_3)(OH)_2 \end{array}\right.$
Erythrin, ...	$\left.\begin{array}{r} C_6H_2(CH_3)(OH)_2.CO.O \\ HO \\ HO \\ C_6H_2(CH_3)(OH)_2.CO.O \end{array}\right\} C_4H_6^{(iv)}$
Picro-erythrin, . . .	$\left.\begin{array}{r} C_6H_2(CH_3)(OH)_2.CO.O \\ HO \\ HO \\ HO \end{array}\right\} C_4H_6^{(iv)}$
Erythrol, ...	$\left.\begin{array}{r} HO \\ HO \\ HO \\ HO \end{array}\right\} C_4H_6^{(iv)}$

---

[1] Homologues of these bodies are obtainable from certain lichens. Thus homoerythrin, $C_{21}H_{24}O_{10}$, has been found in a stunted specimen of *Rocellia fuciformis*. Evernic acid, $C_{17}H_{16}O_7$, occurring in *Evernia Prunastri;* and usnic acid, $C_{18}H_{18}O_7$, and barbatic acid, $C_{19}H_{20}O_7$, found in *Usnea barbata*, are homologous with orsellic acid, and split up in a similar manner when boiled with alkalies.

Picroerythrin, $C_{12}H_{16}O_7$, is only slightly soluble in cold water, but very readily in hot, and on cooling the solution is deposited in silky needles or shining plates, melting at 158° C., and having at once a slightly sweet and intensely bitter taste. With ammonia, ferric chloride, and basic and neutral lead acetate it reacts like erythrin. Its behaviour when boiled with alkalies has already been described.

Lecanoric, Orsellic, or Diorsellinic Acid. $C_{16}H_{14}O_7$. This substance bears the same relation to orcellinic acid that tannic acid (digallic acid) bears to gallic acid (page 87). It may be obtained by extracting the lichen *Rocella tinctoria* with ether, evaporating the solution, treating the residue with milk of lime, again filtering, precipitating the filtrate with sulphuric acid, and crystallising the precipitated orcellic acid from alcohol. It is scarcely soluble in cold water, and requires 2500 parts of boiling water for solution, but dissolves more readily in alcohol and ether. It forms prismatic needles containing 1 *aqua*, which become anhydrous at 100°, and melt at 153° C. with decomposition and evolution of carbon dioxide. The alcoholic solution of lecanoric acid gives no precipitate with lead acetate, but yields with cupric acetate a pale green precipitate after standing. Ferric chloride produces a dark purple-red colour, and ammonio-nitrate of silver is reduced on heating. When boiled with water, lecanoric acid undergoes hydrolysis, and is converted into orcellinic acid, $C_8H_8O_4$. Boiled with alcohol it yields ethyl orcellinate (pseudo-erythrin).

Orcellinic Acid. Dihydroxytoluic Acid. $C_6H_2(CH_3)(OH)_2.COOH$. [$COOH:OH:CH_3:OH_2=1:2:4:5$]. This substance results from the hydrolysis of lecanoric acid (see above), but is best prepared by heating erythrin on the water-bath with baryta-water, until barium carbonate begins to separate. When a sample no longer gives a gelatinous precipitate on adding hydrochloric acid, the liquid is acidulated, when orcellinic acid gradually precipitates. It can be crystallised from acetic acid or dilute alcohol in stellate masses, which contain 1 *aqua*, become anhydrous at 100°, and melt with partial decomposition at 176° C. Orcellinic acid is readily soluble in water, the solution gradually decomposing into orcinol and carbon dioxide when boiled alone or with alkalies. It is coloured a purple-violet by ferric chloride, and yields an amorphous precipitate with ammoniacal acetate of lead.

Orcellinic acid is characterised by the great facility with which it forms ethers. Thus amyl orcellinate is readily formed by boiling erythrin (erythryl orcellinate) with amyl alcohol, and ethyl ocellinate, $C_8H_7O_4(C_2H_5)$, formerly called pseudo-erythrin, is always obtained when lichens containing erythrin are extracted with boiling alcohol. It is slightly soluble in cold water, more readily in hot water or alcohol, and crystallises in small needles or plates, which melt at 132°. The aqueous solution is precipitated by lead acetate.

ERYTHROL, ERYTHRITE, or ERYTHROGLUCIN. $C_4H_6(OH)_4$. This substance, which has the constitution of a tetratomic alcohol, is a product of the decomposition of picroerythrin by alkalies, and exists ready formed in the *Protococcus vulgaris.* It crystallises in colourless dimetric prisms, fusing at 120° C. It is readily soluble in water, sparingly in alcohol, and insoluble in ether. Erythrol has a slightly sweet taste, is optically inactive, and does not reduce Fehling's solution. When distilled with excess of strong hydriodic acid, it yields butyl iodide, C_4H_9I. By treatment with a mixture of strong nitric and sulphuric acid, it is converted into tetranitro-erythrol, $C_4H_6O_4(NO_2)_4$, a body having marked explosive properties. By prolonged treatment with nitric acid, erythrol is converted into oxalic acid, no mucic acid being simultaneously formed.

ORCINOL. ORCIN. Dihydroxy-methylbenzene. $C_6H_3(CH_3)(OH)_2{}^m$. This substance, which is homologous with resorcinol, and has the characters of a diatomic phenol, occurs in a free state in various species of lichens, and is a decomposition-product of the various acids and ethers contained in or prepared from these plants. It is best prepared by boiling erythrin (prepared as described on page 315) for half an hour with a slight excess of milk of lime, in an apparatus furnished with an inverted condenser, filtering, passing carbon dioxide through the filtrate, and evaporating the solution nearly to dryness. On agitating the concentrated liquid with hot benzene the orcinol is taken up, and can be obtained by separating and evaporating the solvent, while the erythrol remains in the aqueous layer. Orcinol may also be obtained by synthetical means.

Orcinol forms six-sided monoclinic prisms, melting at 58°, and containing $C_7H_8O_2+H_2O$. The crystals effloresce gradually over sulphuric acid, and more rapidly when heated to 100°. The anhydrous substance melts at about 107°, and distils with some decomposition at about 287° under atmospheric pressure, but may be obtained pure and colourless by distillation *in vacuo.* When pure, orcin is colourless, but it acquires a pale reddish-brown colour on exposure to air. It has an intensely sweet, but unpleasant, astringent taste. Orcinol is extremely soluble in hot water, but much less so in cold. It is almost completely precipitated in fine needles when its concentrated solution is warmed with saturated brine. Orcin dissolves readily in alcohol and ether, but less easily in hot benzene. The crystals deposited from the ethereal solution are anhydrous. It is neutral in reaction, but possesses marked acid properties. It readily decomposes sodium carbonate, and precipitates silica from silicates.

With oxidising agents orcinol yields oxalic acid. With concentrated sulphuric acid it gives a sulphonic acid. When treated with a solution of bleaching powder, orcin yields an intense purple-red coloration, which rapidly changes to yellow. The most minute trace of orcin may be detected by this reaction.

When an aqueous solution of orcin is mixed with ammonia and exposed to the air it acquires a deep purple colour, owing to the formation of a body called orceïn, identical with the colouring matter of *archil*. If carbonate of sodium or potassium be also present, a blue colouring matter is formed which is identical with that contained in litmus.

If an alkaline solution of orcinol be heated with a little chloroform, it becomes first purple-red and then bright red, and on dilution with water exhibits an intense greenish-yellow fluorescence, from the formation of homofluoresceïn, $C_{23}H_{18}O_5$. This reaction, first observed by Schwartz (*Berichte*, xiii. 543), is so delicate that the compounds which yield orcinol on treatment with alkalies can readily be detected by this means in the lichens containing them, by simply boiling a few pieces of the plant with a 5 per cent. solution of caustic potash, adding a little chloroform to the clear liquid, then warming the solution for ten minutes more, and diluting it with water.

An aqueous solution of orcinol is not precipitated by mercuric chloride, lead acetate, cupric sulphate, tannin, or gelatin. With basic acetate of lead it yields a white precipitate, and with ferric chloride a violet-black coloration or red precipitate.

On addition of bromine-water to orcinol in aqueous solution, tribromorcinol, $C_7H_5Br_3O_2$, is formed, and the reaction has been recommended by Reymann for the quantitative determination of orcin and the assay of archil weeds. The process is carried out exactly like the volumetric determination of phenol by bromination (vol. ii. page 543).

Orceïn is the product of the action of ammonia and oxygen on orcinol. Liebermann states that two compounds may be thus formed, containing respectively $C_{14}H_{11}NO_3$ and $C_{14}H_{12}N_2O_3$. The latter substance is the chief product when the ammonia is in excess, and is less soluble in alcohol and ammonia than the former compound. Both bodies form brown amorphous masses, having a beetle-green lustre. Orceïn is somewhat soluble in water with red colour, but is reprecipitated from its solution by neutral salts of the alkali-metals. In ether it is insoluble, but dissolves readily in alcohol, yielding a scarlet solution. In fixed alkalies and ammonia orceïn dissolves with formation of splendid purplish-violet solutions.

ARCHIL, ORCHIL, or ORSEILLE is the commercial colouring matter from *Rocella tinctoria* and *R. fuciformis*. It is usually prepared by treating the finely chopped lichens with dilute ammonia, and keeping the mixture at about 20° C. till a dark violet paste has been formed. This when diluted with ammonia and filtered through a press yields *blue archil*, while on gently heating this till the ammonia is removed *red archil* is obtained. *French purple* is a lake obtained by precipitating the ammoniacal liquid obtained as above with calcium chloride. In using it, the colouring matter is treated with oxalic acid and boiled with water. The filtered liquid, when rendered slightly ammoniacal, dyes silk and wool a fine purple colour.

Archil has lost much of its importance since the introduction of the coal-tar dyes, and is now chiefly used in combination with other colouring matters to obtain certain shades of brown, and for the production of a cheap blue on wool, the material being first lightly grounded with indigo and then passed through a bath of archil, when it is dyed a rich purple hue, similar to that produced by indigo alone.

Archil occurs in commerce in two forms, paste and liquor. The solid matter consists essentially of the impure orceïn in combination with ammonia. Archil varies greatly in quality, owing to differences in the weed employed, the care used in the manufacture, and the presence or absence of impurities. In some cases it contains an immoderate excess of ammonia, and in others the proportion of solid matter is abnormally low. This can be readily ascertained by drying a known weight of the sample at 100°. Occasionally the solid matter in archil paste is as low as 20 per cent. Spent weeds, from the manufacture of archil liquor, are sometimes added to the paste.

Archil liquors range in specific gravity from 1·040 to 1·080, or even to 1·100, but the density is no accurate indication of the dyeing power, which is best ascertained by a practical dyeing test on wool.

Archil paste is sometimes adulterated with other vegetable colouring matters. To detect these, J. W. Slater recommends that 3 or 4 grammes of the sample should be treated with 100 c.c. of water, and 50 drops of a solution of stannous chloride in twice its weight of water added. On boiling the liquid, a yellowish colour only will remain if the archil be pure, but 3 to 4 per cent. of logwood liquor will yield a greyish-blue, and the colour will be reddish if peach-wood, sapan-wood, or other red wood has been added as an adulterant.

Archil is decolorised by reducing agents, but the colour returns on exposing the reduced liquid to the air. Its other reactions and the methods of detecting it will be gathered from the description of the methods of detecting it in wine (vol. ii. page 88; iii. 222 *et seq.*), and from the following processes of examining the commercial substance for adulterants.

Archil is now frequently adulterated with aniline dyes, especially magenta, acid magenta, and methyl violet.

H. Crossley (*Jour. Soc. Dyers, &c.*, ii. 23) determines basic magenta in archil by diluting the sample, if necessary, with hot water, filtering, and evaporating the filtrate to dryness at 100°.[1] The residue is reduced to powder, and a weighed portion is digested with strong ammonia, which dissolves the orceïn and leaves the magenta base. The solution is filtered, and the residue is washed with ammonia till no more colouring matter is removed, when it is dried at 100° and weighed. It should be proved to be magenta by dissolving it in dilute acetic acid and applying the ordinary tests (page 221). Another method for the detection of magenta consists in treating the residue obtained by evaporating the filtered solution of the sample on filter-paper with two or three drops of benzoic aldehyde or aniline oil, when the magenta will dissolve and colour the paper crimson. A faint pink tint is obtained with pure archil after a few minutes, but this is not readily mistaken for the immediate and strong coloration given by magenta.

For the detection of magenta or methyl-violet in proportions greater than 1 per cent., E. Knecht (*Jour. Soc. Dyers, &c.*, ii. 58) employs cotton yarn dyed with chrysamine (page 206). This does not take up the colouring matter of archil, but is dyed red by magenta, and brownish-red by methyl-violet. For the determination of magenta in archil, Knecht evaporates the filtered liquid to dryness, extracts the residue with alcohol, filters, and evaporates the filtrate. This second residue is heated for about a minute with caustic soda, and the insoluble portion allowed to settle. After standing a few minutes the liquid is decanted, and the residue treated with a more dilute soda solution, the process is repeated as long as the liquid takes up colouring matter. The residue is then washed with water and weighed. On subsequently treating it with hydrochloric acid, it will dissolve with magenta or violet colour, according to its origin. Safranine and the azo-dyes cannot be detected in this manner.

---

[1] T. Fairley (*Jour. Soc. Chem. Ind.*, v. 286) treats archil paste at once with strong ammonia, repeating the process till all the orceïn is removed.

Liebmann and Studer (*Jour. Soc. Chem. Ind.*, v. 287) test archil for magenta by saturating the largely diluted solution with sulphurous acid, when most of the orceïn is precipitated. On adding acetone to the filtered solution, genuine archil does not show any change of colour, but if either basic or sulphonated magenta be present the liquid changes in a few minutes to violet. One-tenth per cent. of magenta in archil gives a strong coloration. If the liquid which was saturated with sulphurous acid be boiled, filtered, and a piece of cotton, mordanted with tannin and tartar-emetic, immersed in the filtrate, only magenta will be fixed on the fibre, and whether it be the acid or basic kind can be ascertained as described on page 226.

C. Rawson (*Chem. News*, lvii. 165) objects to the foregoing methods on the ground of want of delicacy, and recommends that an amount of archil paste or liquor containing 1 or 2 grammes of solid matter should be boiled with 50 c.c. of alcohol, and the solution diluted with 100 c.c. of water. From 15 to 20 c.c. measure of a solution of basic acetate of lead, of 1·25 sp. gr., is next added, and this is followed after stirring by a similar quantity of strong ammonia. With pure archil, the filtered liquid will be quite colourless, but if magenta be present it may either be colourless or pink, according to the amount of ammonia present in the solution; but in either case, on acidulating the liquid the characteristic colour of magenta will be at once developed, no change occurring with pure archil. By a colorimetric test, using for comparison an aqueous solution of magenta containing 0·001 gramme per 100 c.c. and acidulated with acetic acid, the proportion of magenta present may be determined, but in this case the lead precipitate must be washed with a mixture of 5 parts of alcohol, 10 of water, and 1 of strong ammonia.

The foregoing test also serves for the detection of safranine and methyl-violet. On adding acetic acid to the ammoniacal filtrate, the liquid becomes bluish-violet, if the latter dye be present. Strong ammonia decolorises methyl-violet and magenta, but scarcely affects the colour of a solution of safranine, while strong hydrochloric acid changes the latter to blue, and turns solutions of magenta and methyl-violet yellow.

F. Breinl has pointed out (*Jour. Soc. Dyers, &c.*, iv. 46) that various azo-dyes, producing colours ranging from crimson to claret-red, are now in the market, under such names as orchil extract, orchil-red, orselline, &c., being intended as actual substitutes for archil and cudbear, and, being cheaper than magenta, are more likely to be used for the adulteration of those colouring matters. Breinl gives a very complete list of such coal-tar colours, and a table of reactions by which they may be recognised. He divides them into three groups, according to their behaviour with common salt, and with basic acetate of lead (sp. gr. 1·25) in presence of 25 per cent. of alcohol. Thus, on saturating the aqueous solution of the sample with common salt, the following coal-tar dyes are completely precipitated. Orsellin BB and orchil red B (Bayer & Co.), orchil red A (Bad. Anilin und Soda F.), cloth reds B and G (Oehler), Bordeaux G, BX, and Extra (Bayer), Bordeaux B (Actien Ges. für Anilin Fab.), fast reds A and B (Bad. Anilin und S. F.). The following colours are almost completely salted out by similar treatment:—Azorubin S and orchil red G (Actien Ges. für Anilin Fab.), amaranth, carmoisin B (Bayer), magenta, basic colouring matters from magenta residues, and safranine. On the other hand, acid magenta and other acid colouring matters from magenta-residues, orselline R and B (Höchst Colour-works), and red-violet NRS. (Bad. Anil. und S. F.) are not precipitated by common salt. A filtered extract of archil gives a slight precipitate with salt, which redissolves when washed with brine. The coal-tar dyes which are not completely or partially precipitated by saturating their solutions with common salt may be distinguished from archil by boiling with a solution made by dissolving 10 grammes of crystallised stannous chloride in a mixture of 25 c.c. of concentrated hydrochloric acid and 50 c.c. of water. When thus treated, a filtered solution of orchil or cudbear is decolorised or turned light brown; while acid magenta, acid colouring matters from magenta-residues, and red-violet NRS, acquire a darker and more bluish coloration, and orselline R and B an intense bluish-violet coloration. These colouring matters again are only partially precipitated when a solution containing 25 per cent. by measure of absolute alcohol is treated with basic lead acetate; whereas archil is completely precipitated under these conditions, and the other coal-tar dyes already mentioned are not precipitated at all. By these reactions it is always possible to establish the presence of a coal-tar dye, even if it be not possible to identify it with certainty.

An admixture of brazil-wood, barwood, or logwood with orchil or cudbear may be detected by immersing cotton, mordanted with iron or aluminium (page 278), in the hot dilute solution of the suspected sample.[1] After half an hour's treatment the cloth is removed, and washed with warm soap solution. The orchil or cudbear will produce at most a faint pink colour on the mordanted cotton, and this will be removed by boiling the cotton for a few minutes with alcohol, while if logwood be present, cotton mordants with iron will be dyed bluish-grey or black, and if mordanted with alumina salts bluish-violet. Brazil-wood will dye the iron mordant blackish-brown, and the alumina mordant red.

---

[1] As the colouring matter of barwood is not readily extracted by water, it is best to boil 2 grammes of the suspected cudbear for 10 minutes with 50 c.c. of alcohol, and then dilute the solution with water to 200 c.c.

C. Rawson (*Jour. Soc. Dyers, &c.*, iv. 69) detects azo-dyes in cudbear by sprinkling a little of the sample on some concentrated sulphuric acid, when the formation of a streak of characteristic colours—green, blue, violet, &c.—often affords valuable assistance. To obtain further evidence of the presence of azo-colouring matters, he recommends that 5 to 10 grammes of worsted yarn should be dyed for an hour with about 10 per cent. of its weight in cudbear in a bath rendered faintly alkaline with ammonia. A fresh quantity of yarn is similarly dyed in the partially exhausted bath, whereby the greater part of the orceïn is removed from the solution. Sulphuric acid, equal to 3 per cent. of the weight of the yarn, is now added, and a third quantity of worsted yarn introduced. The azo-red is now deposited on the wool in a form sufficiently pure to allow of its subsequent identification. It is desirable, though not directly necessary, to treat a genuine sample of cudbear side by side with the sample.

Cudbear, called on the Continent *Perseo*, is obtained by the action of ammonia or urine on various kinds of lichen, especially *Lecanoria tinctoria* and *Variolaria orcina*, and hence in its origin and properties is very similar to archil, from which it differs mainly in being free from all excess of ammonia and moisture, and in being reduced to a fine powder. It often contains a considerable proportion of mineral matter, usually common salt, which is sometimes added as an adulterant, but in other cases to reduce an unusually rich article to a uniform standard of quality. Genuine cudbear leaves from 5 to 12 per cent. of ash. Cudbear is liable to much the same organic sophistications as archil, and if it be boiled with water the filtered solution may be examined by the same methods.

Litmus, or *tournesol*, is prepared from various species of *Rocella*, *Variolaria*, and *Lecanoria* by allowing them to ferment in presence of ammonia, as in the manufacture of archil, except that in the case of litmus potassium carbonate is likewise added. When the mass has become violet, stale urine, lime, and potashes are added, and the mass is again allowed to ferment until it assumes a blue colour, when it is mixed with chalk or gypsum and a little indigo, and made up into small tablets.

On extracting litmus with cold alcohol, a red colouring matter is obtained, which is unaffected by acids, and yields litmus-blue and another substance on treatment with water. On evaporating this solution, and treating the residue with absolute alcohol and a little acetic acid, a scarlet colouring matter is removed, which is changed to purple by ammonia, while the pure litmus-blue remains behind as a brown powder, soluble in water to a reddish-brown solution, which is turned blue by the slightest trace of an alkali.

Azolitmin, $C_7H_7NO_4$, the characteristic colouring matter of litmus, may be obtained in a state of purity, according to De Luynes, by digesting 1 part of orcinol with 1 of strong ammonia, 25 of crystallised sodium carbonate, and 5 of water, at 60°–80° C. for four or five days in a closed vessel. A blue liquid is thus obtained, which is diluted with water and slightly acidulated with hydrochloric acid, when a precipitate is formed, which, after being washed and dried, is regarded as pure azolitmin. So obtained, azolitmin is a blue substance, which acquires a coppery lustre by friction. It is nearly insoluble in cold water or benzene, but dissolves in alcohol with red and in ether with yellow colour. Azolitmin appears to have the characters of a weak acid, the salts of which are blue, and the potassium compound of which exists in litmus.

Litmus exhibits a very characteristic absorption-spectrum. Ether extracts it from an acid solution, and forms a yellow liquid, which absorbs the more refrangible end of the spectrum to a point midway between D and E. On adding a drop of ammonia to the ethereal solution the liquid becomes blue, and an absorption-band is formed, which commences at *d*, where it is extremely black, and gradually diminishes to E. On shaking the ethereal solution with ammoniacal water, the colouring matter passes into the aqueous liquid, and the blue solution shows a well-marked absorption-band at D. Addition of acid now changes the colour to red, and the band at D disappears, the spectrum of the acidified liquid resembling that of œnolin, the colouring matter of red wine.

Litmus is not employed in dyeing or calico-printing, but is used for colouring wine and vinegar, and in the laboratory is well known as an indicator of neutrality. Its indications are fairly delicate; but the habit of regarding litmus as an infallible guide to neutrality has seriously retarded progress in several directions.[1] Of late years this fact has been more generally recognised, and a number of other indicators have been proposed. Of these, two—namely, *helianthin* or *methyl-orange* (page 188) and *phenolphthaleïn* (page 164)—deserve the fullest confidence, and one or other of them can be employed advantageously in place of litmus in a large number of cases.

In the following table, by R. T. Thomson (*Journ. Soc. Chem.*

---

[1] Litmus is still employed for the titration of lime and lemon juice, a purpose for which, in the opinion of the author, it is very ill-suited, especially if sodium carbonate be used for the neutralisation (see *Analyst*, xiv. 25, 80).

Ind., vi. 198), is given an epitome of the indications yielded by litmus, as compared with those given by phenolphthaleïn and methyl-orange (which last is affected by strong acids only). The figures represent the number of atoms of hydrogen displaced by sodium or potassium in the form of caustic alkali, when a compound is formed having a neutral reaction to the indicator in question. Thus, when methyl-orange is used in the titration of sulphurous acid the neutral point is reached when alkali has been added in quantity sufficient to form the compound $NaHSO_3$; but when phenolphthaleïn is used the point of neutrality corresponds to the formation of the salt Na_2SO_3. By a combined use of the two indicators valuable volumetric determinations can be effected. In employing phenolphthaleïn as an indicator, it must be remembered that the results are vitiated by the presence of ammonium salts. In other cases, when a blank space appears in the table, it is meant that the end-reaction is obscure, and not to be depended on.

The table shows the basicity of acids with different indicators, when titrated in aqueous solution with fixed caustic alkali.

Acids.		Methyl Orange.	Phenolphthaleïn.		Litmus.	
Name.	Formula.	Cold.	Cold.	Boiling.	Cold.	Boiling.
Sulphuric, . .	H_2SO_4	2	2	2	2	2
Hydrochloric, .	HCl	1	1	1	1	1
Nitric, . .	HNO_3	1	1	1	1	1
Thiosulphuric, .	$H_2S_2O_3$	2	2	2	2	2
Carbonic, . .	H_2CO_3	0	1 dilute	0	...	0
Sulphurous, .	H_2SO_3	1	2	...	...	...
Hydrosulphuric,	H_2S	0	1 dilute	0	...	0
Phosphoric, .	H_3PO_4	1	2	...	...	...
Arsenic, . .	H_3AsO_4	1	2	...	...	...
Arsenious, . .	H_3AsO_3	0	...	...	0	0
Nitrous, . .	HNO_2	indicator destroyed	1	...	1	...
Silicic, . .	H_4SiO_4	0	...	...	0	0
Boric, . . .	H_3BO_3	0	...	...	...	...
Chromic, . .	H_2CrO_4	1	2	2	...	...
Oxalic, . .	$H_2C_2O_4$	...	2	2	2	2
Acetic, . .	$HC_2H_3O_2$	...	1	...	1 nearly	...
Butyric, . .	$HC_4H_7O_2$	...	1	...	1 nearly	...
Succinic, . .	$H_2C_4H_4O_4$	...	2	...	2 nearly	...
Lactic, . .	$HC_3H_5O_3$	...	1	...	1	...
Tartaric, . .	$H_2C_4H_4O_6$	...	2	...	2	...
Citric, . .	$H_3C_6H_5O_7$	...	3	...	...	...

It will be seen that all indicators behave alike on titrating strong mineral acids with fixed caustic alkali; in the titration of a weak acid with a strong base they differ, methyl-orange being most sensitive to alkalies and phenolphthaleïn to acids, while litmus occupies an intermediate place. Speaking generally, lacmoid (page 159), dimethylamido-azobenzene (page 180), cochineal, and congo-red (page 206) behave like methyl-orange, while turmeric behaves like phenolphthaleïn.[1] Phenacetolin and rosolic acid (page 161) usually react like litmus, except that in the latter case a sharp neutrality-point is obtained in titrating sulphurous acid when the salt Na_2SO_3 is formed.

Red Dyes from Woods, &c.

A number of red colouring matters of vegetable origin are, or have been, used in dyeing. Thus, *madder* is the root of *Rubia tinctorum*, a herbaceous plant. Its cultivation is almost obsolete, and its characters have already been sufficiently described. Other red colouring matters, as *logwood* and *brazil-wood*, are obtained from the wood of trees of considerable size; while *alkanet* is obtained from the cortical parts of a root, and *safflower* from the flowers of a

Commercial Name.	Botanical Origin.	Geographical Origin.	Colouring Principle.	
			Name.	Formula.
Madder.	Root of *Rubia tinctorum*.	Turkey, France, Holland.	Alizarin. Purpurin.	$C_{14}H_8O_4$ $C_{14}H_8O_5$
Logwood or Campeachy wood (page 328).	Wood of *Hæmatoxylon campechianum*.	West Indies, Mexico, South America.	Hæmatoxylin. Hæmateïn.	$C_{16}H_{14}O_6$ $C_{16}H_{12}O_6$
Brazil wood; Pernambuco wood (page 333).	Wood of *Cæsalpinia Brasiliensis* and *C. Crista*.	Brazil, Pernambuco, Jamaica.	Brazilin.	$C_6H_{14}O_5$
Peach wood (page 333).	Wood of *Cæsalpinia echinata*.	Nicaragua, Sierra Nevada.	Do.	Do.
Sapan wood (page 333).	Wood of *Cæsalpinia sapan*.	Siam, Japan, East Indies, &c.	Do.	Do
Sandal, Santal, or Sanders wood (page 335).	Wood of *Pterocarpus santalinus*.	East Indies, Ceylon, Madagascar.	Santalin.	$C_{15}H_{14}O_5$ (?)
Barwood (page 336).	Wood of *Baphia nitida*.	Sierra Leone.	Do.	Do.
Camwood, or Kambe wood (page 336).	Wood of species of *Pterocarpus*.	West coast of Africa.	Do.	Do.
Alkanet (page 337).	Root of *Anchusa tinctoria*.	Levant, South Germany.	Alkannin.	$C_{15}H_{12}O_4$, or $C_{15}H_{14}O_4$
Safflower (page 338).	Flowers of *Carthamus tinctoria*.	Southern Europe, South America, East Indies.	Carthamin.	$C_{14}H_{16}O_7$

---

[1] Thus saliva and milk are neutral to litmus paper, strongly alkaline to lacmoïd or congo-red, and acid to turmeric paper.

kind of thistle. The preceding table (page 327) shows the origin of the more important red colouring matters derived from plants.

LOGWOOD or CAMPEACHY (see page 328) is the most important of the red dye-woods,[1] and is imported in the shape of irregular blocks, having an average weight of about 400 pounds. The colouring matter probably exists in the form of a glucoside, for when the trees are freshly felled the wood is colourless. By the time the logs arrive in this country they have acquired a dark brownish-red colour externally, while the inside is still pale yellow or light red. The logs are reduced to chips or raspings, which are moistened with water and allowed to ferment, whereby the glucoside is converted into hæmato-xylin, and this is partially converted into hæmateïn by the action of the air. The product is lixiviated with water, and the solution concentrated to obtain a *logwood extract*. To obtain a good extract, the powder must not be too highly oxidised, and the concentration of the solution must be conducted at a temperature not exceeding 60° C., or the hæmateïn will be converted into a dark purple resinous matter which injuriously affects the brilliancy of the colour. An inferior extract is largely made from campeachy *roots*.

Logwood yields very little soluble and colouring matter to cold water, but from 14 to 18 per cent. of its weight to boiling water. The decoction is pale yellow if made with distilled water, but blood-red if a calcareous water has been employed. The whole of the hæmatoxylin can only be removed with difficulty by water, but alcohol and ether extract it with facility.

Hæmato-xylin,[2] $C_{16}H_{14}O_6$, is best obtained by treating the aqueous extract of logwood, or the finely powdered wood, with ether, evaporating the resultant solution to a syrup, adding water, and allowing it to stand for some days, when the hæmatoxylin is deposited in crystals, which if prismatic contains 3 *aqua*, but if granular 1 *aqua* only. A portion of the water is lost at 100°, but the whole of it can only be expelled at a higher temperature. When further heated, hæmatoxylin fuses, and at a still higher temperature decomposes and leaves a bulky carbonaceous residue. The crystals of hæmatoxylin are bright yellow, sometimes brownish externally, but the powder is yellowish-white. Its taste resembles that of liquorice.

Hæmatoxylin is only slightly soluble in cold water, but more readily on heating, and is dissolved with facility by alcohol, ether, and carbon disulphide. It has the characters of a weak acid, and unites with bases to form compounds which are colourless when perfectly pure, but absorb atmospheric oxygen with great avidity, becoming first bluish and finally reddish-brown, from formation of hæmateïn and more advanced products of oxidation. The compounds of hæmatoxylin with the alkalies are best obtained by saturating a cold decoction of freshly-drilled logwood with common salt, and gradually adding caustic soda. The precipitate first formed contained the coloured oxidation-products, and should be rapidly filtered off, and on again adding caustic soda a colourless precipitate of the sodium salt is obtained, which becomes rapidly coloured on exposure to air.

---

[1] For convenience of classification, logwood is here classed as a red dye-wood. Although the colouring matter of logwood is itself red, it is not used in practice to produce red shades, but rather violet, blue, and black.

[2] This word is often pronounced hæmat-oxylin, but such a practice is open to objection.

Neutral and basic acetates of lead yield, with hæmatoxylin, bluish-white precipitates, which rapidly darken on exposure to air. Stannous chloride produces a permanent rose-coloured precipitate. Alum gives a bright red colour, but no immediate precipitate, though a slight blackish precipitate is formed after some time; and aluminium acetate yields a fine purple. Hæmatoxylin instantly reduces chromic acid and potassium bichromate, yielding a deep black precipitate.

Hæmateïn, $C_{16}H_{12}O_6$, is produced with great facility by the atmospheric oxidation of hæmatoxylin, especially in presence of an alkali. It may be prepared by saturating ammonia with hæmatoxylin, and exposing the warm solution to the air. The liquid becomes deep cherry-red, and ultimately deposits granular crystals of the ammonium salt of hæmateïn. This, when decomposed by acetic acid, yields free hæmateïn as a bulky, brownish-red precipitate, which on drying becomes deep green, and exhibits a metallic lustre. Hæmateïn yields a red powder, which is sparingly soluble in cold but more readily in boiling water. It is sparingly soluble in alcohol and acetic acid and slightly soluble in ether, and dissolves in ammonia and the fixed alkalies to form solutions which are at first blue or purple, but become brown by contact with air. The ammonium salt forms a deep violet powder, consisting of microscopic, transparent, four-sided prisms, which dissolve in water with purplish, and in alcohol with reddish-brown colour. The salt loses its ammonia at 100° C., or even at the ordinary temperature over sulphuric acid *in vacuo*. Its solution yields a violet-blue precipitate with salts of copper, and a violet with stannous chloride. It reduces silver nitrate, and with ferric salts gives a black precipitate. By oxidising agents hæmateïn is converted into brown ulmic bodies. By sulphuretted hydrogen it is decolorised, but hæmatoxylin is said not to be the product of the reduction, though it is certainly formed when sulphurous acid and certain other reducing agents are employed.

Hæmateïn is destroyed by hot sulphuric acid, but dissolves in the cold concentrated acid, with dark reddish-brown colour. On adding two or three measures of glacial acetic acid very gradually to this solution, a body of the formula $C_{16}H_{11}(SO_3H)O_6$, is thrown down as an orange crystalline precipitate. This body, which is apparently a sulphonic acid, is insoluble in alcohol, ether, or benzene, but slightly soluble in strong acetic acid or cold ammonia.

The reactions of an aqueous decoction of logwood are due to the simultaneous presence of both hæmatoxylin and hæmateïn.[1] Dilute acids turn the solution yellow, but with excess of a strong acid a red colour is produced. Sulphuretted hydrogen decolorises the solution of logwood, and sulphurous and carbonic acids turn it yellow. Alkalies and ammonia produce first a red, then a violet, and ultimately a brown colour; while lime, baryta, and most of the hydrated oxides of the heavy metals produce blue precipitates. Stannous hydroxide behaves as a base and yields a violet lake, while stannic hydroxide reacts as an acid and turns logwood solution red. Salts of iron yield a bluish-black coloration, a reaction which is employed for producing *ink*. Mercuric chloride yields an orange, tartar-emetic a carmine, and bismuth nitrate a fine violet precipitate with logwood solution. Alum gives at first a yellow coloration, becoming red after a time; while aluminate of sodium yields an abundant bluish-violet precipitate, insoluble in excess of alkali. This reaction is said to be so delicate and characteristic that by means of it logwood may be detected in a mixed decoction with great facility. Another characteristic reaction of logwood is the black coloration it produces with bichromate of potassium. A good way of applying the test is to boil some white wool in a solution of potassium bichromate, containing such an amount of the salt as will correspond to 3 per cent. of the weight of the wool. The mordanted wool is then introduced in small successive portions into the hot liquid to be tested, when it will be dyed black if logwood be present, and the weight which can be thus dyed will be an indication of the amount of colouring matter. This method of assay takes cognisance both of the actual and potential colouring matter present (hæmateïn and hæmatoxylin), and, as pointed out by L. Siebold (*Jour. Soc. Chem. Ind.*, 1889), is a more rational method of examination than any based on the colour produced on cotton mordanted with alumina or tin salts.

---

[1] C. E. Avery (*Jour. Soc. Dyers, &c.*, i. 268) has patented the use of hypochlorites, nitrates, chlorates, &c., for oxidising hæmatoxylin to hæmateïn, and thus getting the full development of colour without "ageing."

The colouring matter of logwood may be extracted by agitating the acidulated aqueous solution with amylic alcohol, or, less advantageously, with chloroform. On shaking the amylic alcohol with a saturated solution of borax, the colouring matter passes into the latter, and may be isolated by separating the borax solution, acidulating it, and again shaking with amylic alcohol.

In commerce, logwood chips or raspings often occur containing an abnormal proportion of *water*, from 40 to 50 per cent. being occasionally met with. 14 per cent. is the average proportion of water natural to unfermented logwood, and should be deducted in calculating the excess. An excess causes fermentation when the material is allowed to remain long in heaps, with consequent destruction of the colouring matter.

Logwood is occasionally treated with an *alkali*, such as lime water, weak soda, or stale urine, with the view of giving it a factitious strength. If so treated, the wood yields abundance of colour to water, but oxidation and deterioration speedily occur. On treating such logwood with a little cold distilled water, and floating a piece of sensitive red litmus paper on the surface of the liquid, the paper will be turned blue before its colour is affected by the logwood.

A rough comparative test of the tinctorial value of logwood may be made by treating 0·5 gramme of each sample with 50 c.c. of methylated spirit, agitating at intervals for an hour, and comparing the depth of colour of the different tinctures.

Logwood extract is met with in commerce both in a liquid and a solid form. The specific gravity is not a reliable indication of the strength of the fluid extract, as it is liable to be raised by the addition of salt, glucose, molasses, &c. The solid and paste extracts may not only contain salt, but are sometimes adulterated with farina, chestnut-bark extract, &c. Treatment of the sample with methylated spirit, and observation of the intensity of the colour of the resulting tincture, is a useful method of examination.

H. Trimble (*Jour. Soc. Dyers, &c.*, i. 92) recommends that the colorimetric assay of logwood extract should be made by treating a volume of solution corresponding to 0·001 gramme of the *dry* extract with 10 c.c. of water naturally or artificially containing "traces of calcium carbonate" and a solution of 0·002 gramme of crystallised copper sulphate. The mixture is brought quickly to the boiling point, and diluted with distilled water to 100 c.c. The colour of the solution is then compared with one of pure hæmatoxylin similarly treated, or with a standard sample of logwood extract.

The most satisfactory method of assaying logwood and logwood extracts is by a miniature dye-test with wool and potassium bichromate, as described on page 330. A known quantity of the sample should be boiled with water, the solution strained, and diluted to a definite volume. A standard specimen must of course be treated in a similar manner, side by side with the sample.

With the exception of indigo, logwood is, perhaps, the most important and indispensable of dyeing matters. It does not dye cotton without a mordant, and wool merely acquires a useless drab-tint. Hence the employment of logwood in dyeing depends on the colour-lakes which it forms with metallic oxides.

With aluminous mordants, logwood yields deep violet-grey shades. With ferrous salts it gives a bluish-black, and with ferric salts a brown-black shade, while a mixture of the two yields a finer black than either separately. With chromates, logwood yields a black colour, which on exposure to light gradually takes a greenish shade. Logwood is used chiefly for dyeing black in conjunction with potassium bichromate. It likewise yields blues, which resemble those produced by indigo, but are not so fast. It is also likewise in dyeing leather, and in printing calico brown, slate, lilac, grey, &c.

Fibres dyed black by logwood leave on ignition an ash containing oxide of chromium, sometimes mixed with alumina or oxide of copper or iron. The dyed fabric is turned red by moderately concentrated hydrochloric acid (tannin blacks are altered, but not reddened), and if the reddened spot be pressed, while still moist, against a piece of filter-paper, it produces a cherry-red stain, which turns blue if touched with a glass rod moistened with aluminate of sodium. Logwood violets and blues leave on ignition an ash containing alumina. With hydrochloric acid they behave like logwood black. When placed in milk of lime, and subsequently washed with soap, the colour is discharged. All logwood colours are readily bleached by chlorine and hypochlorites.

If a fibre dyed with logwood (especially the blues) be boiled with glacial acetic acid the colouring matter is dissolved, and the solvent when cold has a rose-red colour, changing to yellowish-red on warming. On adding ether and sufficient water to cause separation of an ethereal layer, any indigo will remain in the ether or separate at the junction of the two liquids, while in presence of any quantity of logwood the lower layer will be reddish-blue. If the amount present be insufficient to produce this effect, the logwood will still be detected on adding a few drops of hydrochloric acid. This will colour the aqueous liquid a beautiful red, while at the same time it will decolorise that portion of the logwood colouring matter which was taken up by the ether. In the presence of cotton-blue or indigo-carmine, the acetic solution should be separated from the ethereal layer and shaken with amylic alcohol. This dissolves the logwood colouring matter, which can be extracted by agitating the amylic alcohol with a saturated solution of borax, and thus obtained pure.

BRAZIL WOOD is derived from the *Cæsalpinia Brasilienses*, a tree growing in the forests of Brazil (page 327). The red dye-woods known in commerce as *peach-wood*, *sapan-wood*, *Lima-wood*, *Bahia-wood* (page 327), &c., are all the products of various species of *Cæsalpinia*, and yield very similar shades of colours on fabrics, either when employed alone or with mordants. They appear, also, to contain the same glucoside, which is decomposed by peculiar ferments or by boiling with dilute acids into a glucose and the colouring matter brazilin, a substance which has been found in large crystals in casks in which extract of sapan-wood had been kept. The crust obtained in the manufacture of brazil-wood extract contains much brazilin and its lime-compound. If treated with dilute hydrochloric acid, and then boiled with a mixture of one part of alcohol and eight of water, a solution is obtained from which brazilin crystallises on cooling.

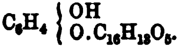
Brazilin, $C_{16}H_{14}O_5$, may be obtained from brazil-wood by the method employed for the preparation of hæmatoxylin from logwood (page 328). When pure it forms colourless hydrated crystals, which become anhydrous at 130° C. It dissolves in water, alcohol, and ether. Brazilin presents a close resemblance to hæmatoxylin, $C_{16}H_{14}O_6$, from which it differs only by an atom of oxygen.[1] On exposure to the air the solution acquires a bright red colour from the formation of brazileïn. This change is greatly facilitated by the presence of alkalies. Acetyl- and bromo-derivatives of brazilin have been obtained.

On adding chromic acid or potassium bichromate to an aqueous solution of brazilin, a dark brown coloration is produced, and a very dark crimson lake separates on standing. This substance, which is apparently a compound of brazilin and chromic oxide, is readily decomposed by dilute acid.

Brazileïn, $C_{16}H_{12}O_5$, is produced by the oxidation of brazilin in alkaline solution, and may be prepared in a manner similar to that used for obtaining hæmateïn, $C_{16}H_{12}O_6$, to which it presents a close analogy. Brazileïn forms minute crystals, having a grey lustre. The powder is reddish-brown. It is very slightly soluble

---

[1] According to E. Kopp, brazilin has the formula $C_{22}H_{18}O_7$, which, if correct, would render it probable that brazilin was the resorcinol ether of hæmatoxylin,



$C_6H_4\left\{\begin{matrix}OH\\O.C_{16}H_{13}O_5\end{matrix}\right.$.

in cold, but more readily in hot water. The solution is yellowish-pink, with a greenish-orange fluorescence. On addition of an alkali the solution becomes carmine-red, changing to brown on exposure to air. With concentrated sulphuric, hydrochloric, and hydroromic acids, brazileïn reacts to form crystallisable compounds, which have greater tinctorial power and are faster on the fibre than brazileïn itself. Boiling with zinc-dust or acid sulphite of sodium reduces brazileïn to brazilin.

An aqueous decoction of brazil-wood, or any of the allied woods, becomes yellow or orange on addition of an acid, the shade of colour depending on the relative proportions of brazilin and brazileïn present. If the solution be strong, yellow or red crystals will probably separate on standing. With excess of strong hydrochloric acid, brazil-wood solution becomes a bright pink, but the coloration disappears on adding water. Ammonia, caustic alkalies, and carbonates of the alkali-metals turn the solution crimson-red, this colour gradually changing to brown on exposure to air. Potassium bichromate reacts as with brazilin (page 33). Neutral lead acetate gives a slight reddish precipitate containing oxidation-products. The filtered liquid dyes a deeper shade than the original solution. Basic acetate of lead gives an abundant bluish precipitate with brazil-wood solution.

Brazil-wood and the commercial extract are liable to the same kind of adulterations as logwood and its preparations, and may be examined by exactly similar methods, except that for the dyeing test twice the quantity of brazil-wood should be employed, as it is not so rich in brazilin as logwood is in hæmatoxylin.

Brazil-wood is used in calico-printing and dyeing, and yields colours similar to those obtainable with cochineal or alizarin. Thus when mordanted with alumina it gives red, with iron greyish-violet or black, and with a mixture of the two, brown. Stannic chloride gives a red, and chromates an olive shade.

When fixed on fabrics, reds produced by brazil-wood are turned violet-blue by alkalies, while acids change them to yellow and red, and give a pink solution. They are bleached by chlorine and hypochlorous acid, and are discharged by boiling with soap solution bluish-red, a character which distinguishes them from the alizarin reds. When immersed in succession in hydrochloric acid and in lime-water, fibres dyed red with brazil-wood are changed to violet, and the latter colour can then be removed by boiling with soap. Concentrated sulphuric acid alters brazil-wood red to deep cherry-red, while it changes a cochineal red to an orange-yellow. On ignition, fibres dyed with brazil-wood leave a residue containing alumina, oxide of tin, &c., according to the mordant employed for fixing the colour.

SANTAL WOOD, BARWOOD, CALIATOUR WOOD, and CAMWOOD (see also page 327) differ from Brazil-wood and its allies in their more resinous character, and are often known as "close woods." They yield faster dyes than the "open woods," but the insolubility of the colouring matters prevents them from being used in the form of extracts.

Santalin, $C_{15}H_{14}O_5$ (?), the colouring principle of santal wood, seems to be identical with that of barwood, and probably with that of camwood. It appears to be developed by age, being absent from the young branches, but existing in large quantity in the trunk. The chemistry of santalin is very imperfectly understood, and the formula is uncertain. Santalin is best extracted by boiling crushed santal wood with water to remove the tannin, heating the insoluble residue with a solution of borax, and saturating it with lime until the colouring matter is entirely removed. The filtered liquid is then treated with sulphuric or hydrochloric acid until no further precipitate is obtained. The voluminous red precipitate is filtered off and dissolved in boiling alcohol, when the santalin separates as a red crystalline powder as the solution cools. Santalin is insoluble in water, but soluble in alcohol, ether, and acetic acid. It dissolves in ammonia, fixed caustic alkalies, and carbonates, phosphates, and borates of the alkali-metals with violet-red colour, and is reprecipitated in red flakes on acidulating these solutions.

A. Zander (*Jour. Soc. Dyers, &c.*, iv. 496) has recently proposed the employment of a santalin-sulphonic acid. This is prepared by treating santal wood, or one of the allied woods, with a warm solution of borax, sodium phosphate, or carbonated or caustic soda, and precipitating the crude santalin from the liquid by means of an acid. The santalin is then warmed with ordinary concentrated or fuming sulphuric acid, until a sample ceases to be precipitated on dilution with water. The product is then poured into a cold, saturated solution of common salt, and the precipitated colouring matter washed and dried. Santalin-sulphonic acid and its sodium salt occur in commerce as greyish-brown powders, readily soluble either in hot or cold water. The solution gives no characteristic reactions. It is best applied in an acid bath containing sodium sulphate, and produces shades of colour much yellower than, but equally deep and fast with, those obtained with the original dye-wood.

Santal Wood or *Sandal Wood* (page 327), called also *sanders wood* or *red sanders*, is imported in large billets, which are very dense (sp. gr. 1·014) and compact, and of blackish-brown colour externally, while the interior is red. The fibres occur in alternate layers running in opposite directions, and hence when planed the wood exhibits alternately a polished and a rough torn-up surface. Powdered santal wood is lighter than water, has an aromatic taste, and an odour like that of orris-root. It yields to alcohol about 16 per cent. of a colouring matter which is insoluble in water.

Santal wood is chiefly used on the Continent, where it is employed to give a bottom to woollen cloth which is afterwards to be dyed with indigo. The fine colour called *bleu de Nemours*, obtained in this manner, has a purple hue by reflected light. Santal wood is also used for dyeing woollen and cotton a dark red, which is changed to a rich brown by a chromate-bath. It produces dark browns with sumach and light browns with fustic.

Barwood is allied to santal wood. It is compact, and of an orange colour when polished. It generally occurs in the form of raspings, as a rough, harsh, and odourless powder. Boiling water takes up about 7 per cent. of colouring matter, which on cooling is almost entirely deposited as a reddish powder. The colouring matter is soluble in alcohol, but the whole amount, averaging 23 per cent., can only be extracted from the wood by repeated treatment. The colouring matter dissolves in soda or ammonia with violet-red colour, and is reprecipitated in red flakes on acidulating the solution.

Barwood is employed to produce mock turkey-reds on cotton, which are distinguished from the alizarin-dyed goods by yielding part of their colour to soap, and at the same time assuming a purple hue. It is also used for dyeing woollens brown and other dark tints.

Cam Wood or *Kambe Wood* yields its colouring matter to water much more freely than santal and barwood, but is not sufficiently soluble to yield an extract. It is used in a manner similar to barwood, and is regarded as producing brighter and faster colours.

An alcoholic extract of santal or barwood is rendered opalescent by copious dilution with water. The fixed alkalies redissolve the precipitate, the liquid acquiring a dark claret colour. Caustic alkalies change the original alcoholic solution to crimson or violet, while lime water produces an abundant reddish-brown precipitate. Dilute acids heighten the colour of an alcoholic solution of santal or barwood to a deep cherry-red; while chlorine decolorises the tincture, with formation of an ochreous precipitate which rises to the surface of the liquid. The tincture of santal or barwood yields with stannous chloride a blood-red, and with stannic salts a brick-red precipitate; with ferrous salts a violet coloration and abundant violet precipitate; with ferric salts an intense brownish-red coloration and precipitate; and with tartar-emetic an abundant, dark cherry-red precipitate. Salts of aluminium only render the liquid turbid, while lead salts give a dark violet, gelatinous precipitate. The last two reactions distinguish santal- and bar-wood from *cam-wood*, an alcoholic extract of which gives a beautiful red coloration with salts of aluminium, and a bright orange-red precipitate with salts of lead.

Santal-, bar-, and cam-wood are chiefly used in wool-dyeing, together with other dyewoods, such as logwood and old fustic, for producing various shades of brown, olive, drab, &c. They have also a limited application in cotton-dyeing, but are not used for silk.

Fibres dyed with santal- or bar-wood are not changed by hydrochloric acid, but if of wool are turned dark olive by nitric acid. Alcohol is coloured red, as also is an acid solution of stannous chloride, the colour of the fibre remaining unchanged. Caustic soda and ammonia turn the fibre purplish or brownish without yielding a coloured solution. When boiled with ferrous sulphate, cloth dyed with santal-wood becomes violet.

ALKANET (page 327) consists of the cortical parts of the root of *Anchusa tinctoria.* The colouring matter called *alkannin* may be prepared by boiling the root with water to remove all soluble matter, drying it, and then exhausting with alcohol. The solution, which has a violet colour, is slightly acidulated with hydrochloric acid and evaporated to dryness. The residue is treated with ether, which on evaporation leaves the colouring matter as a dark red, resinous substance. According to Carnelutti and Nasini (*Jour. Chem. Soc.*, xl. 53), the product so obtained is contaminated with a reddish-brown acid. The colouring matter is best obtained pure by extracting alkanet root with dilute potash solution, and agitating the solution with ether to remove the above-mentioned impurity. On saturating the alkaline liquid with carbonic acid the alkannin is precipitated, and may be purified by solution in ether.

Alkannin, Anchusin, or *Anchusic Acid.* This body, of which the formula is probably either $C_{15}H_{14}O_4$ or $C_{15}H_{14}O_4$, is a reddish-brown resinous substance of metallic lustre. It is insoluble in water, but soluble in alcohol, glacial acetic acid, ether, chloroform, carbon disulphide, turpentine, and fixed oils. The alcoholic solution is crimson, and is unchanged by exposure to light or continued boiling. It gives a blue coloration with alkalies (restored to crimson by acids), a bluish-violet precipitate with aluminium acetate, a crimson precipitate with stannous chloride, and a purple precipitate with stannic chloride. Lead acetate produces a blue, and iron salts a violet precipitate. Alkannin forms a diacetyl-derivative which crystallises from glacial acetic acid in brownish-yellow grains. Alkannin is evidently a derivative of methyl-anthracene, $C_{15}H_{12}$, as that hydrocarbon is formed when the colouring matter is distilled with zinc-dust. In its tinctorial properties and absorption-spectrum, anchusin resembles quin-alizarin.

The most characteristic test for alkanet and alkannin is the absorption-spectrum. The solution in amylic alcohol gives the best results, and exhibits three equidistant bands in the blue-green. On adding ammonia these give place to two bands, one nearly coincident with and the other on the red side of the D line (compare vol. i. page 86).

Alkanet root may be assayed by treating it with ether, which should extract not less than 5 per cent. of colouring matter. Alkanet was formerly used for dyeing various shades of violet, lilac, lavender, and yellow, but has been superseded for such purposes. It is used for staining wood crimson, and is employed in perfumery for colouring oils and pomades. An alkaline solution is sometimes used to colour syrups. Tincture of alkanet forms a very good substitute for litmus.

Safflower consists of the bloom or petals of a plant resembling the thistle (page 327), indigenous to Egypt and the Levant, and cultivated in other countries. It varies much in quality, the Egyptian being the richest in colouring matter, and after that the Indian and Chinese. The colour of good safflower is a fiery red; a dull red colour is an indication of bad preparation.

Safflower contains two yellow colouring matters, one of which is soluble in cold water, and exists in considerable proportion (26 to 36 per cent.); the other is insoluble in water, but dissolves in alkaline liquids. Besides these, safflower contains a small proportion of a red colouring matter called carthamin, which is the only constituent of value. The proportion of insoluble yellow colouring matter varies inversely with that of carthamin.

Carthamin, $C_{14}H_{16}O_7$, the red colouring matter of safflower, forms only from 0·3 to 0·6 per cent. of the weight of the flowers. To prepare it, safflower is washed with cold water till no more soluble yellow colouring matter is removed, after which it is treated with water and 15 per cent. of its weight of crystallised sodium carbonate. The solution is strained from the insoluble portion, cotton yarn immersed in it, and the liquid acidulated with citric acid. The cotton takes up the carthamin and an accompanying yellow colouring matter. When washed and treated with a weak solution of sodium carbonate, the carthamin dissolves, while the yellow dye remains fixed on the cotton. On acidulating the solution with tartaric acid, the carthamin is thrown down as a bright red, amorphous precipitate, which, when mixed with a little water, forms the *safflower extract* or paste of commerce.[1] The product may be further purified by solution in alcohol and reprecipitating it by adding water.

---

[1] If the paste be triturated with French chalk and the mixture dried, a product is obtained which is employed as a *rouge*.

Carthamin is insoluble in water or ether, but readily soluble in alcohol. The cherry-red alcoholic solution dyes silk without a mordant, and when allowed to evaporate on glass leaves a varnish which appears red by transmitted light and a beautiful beetle-green by reflected light. On addition of an acid, the alcoholic solution of carthamin becomes yellow, and alkalies also turn it yellow or orange. The colouring matter is consequently very unstable, and even undergoes rapid alteration on exposure to air or when boiled with alcohol or water.

Carthamin has feeble acid characters. The ammonium salt yields, with stannic chloride, a yellowish-brown precipitate, with ferric chloride a brownish-red, and with mercuric chloride a red precipitate.

Carthamin dissolves with red colour in strong sulphuric acid, probably forming a sulphonic acid, for the solution is not precipitated on addition of water.

Safflower is best assayed by a miniature dyeing operation, and by an application of the method already described for detecting and separating any objectionable yellow colouring matter.

Safflower is employed to dye silk, cotton, and linen various shades of pink and red. On fabrics dyed with annatto it produces a scarlet. The use of safflower has much decreased of late years, owing to the competition of the coal-tar colours, but it is still employed for colouring red tape.

On the fibre, a rose, pink, or crimson colour due to safflower is immediately turned pale yellow by a single drop of alkali, and the colour is then destroyed by any further treatment. Weak acids do not affect the colour, but strong acids, chlorine, and sulphurous acid bleach it at once. Alcohol has no action, but ammonia changes safflower pink (on cotton) to a flesh-tint, and ammonium sulphide decolorises it.

Yellow Dyes of Natural Origin.

The yellow colouring matters of natural origin which receive practical applications are all of vegetable derivation. They are of very various origin and character, as will be seen from the tabulated list of the more important on next page.

A number of other vegetable colouring matters might be enumerated, including *Chinese yellow*, from *Gardenia grandiflora; Chrysophan*, from Goa powder (page 281); the colouring matters of rhubarb, barberry root and carrot, and many others.

QUERCITRON BARK, as met with in commerce, is a mixture of fibres and fine powder of a yellow or buff colour. The articles imported respectively from Philadelphia, New York, and Baltimore rank as distinct qualities, the first being generally preferred.

Quercitrin, the yellow colouring principle of quercitron, was obtained by Chevreul by boiling the bark with water, and allowing the solution to stand, when the quercitrin is deposited in crystals. Bolley prepares it by boiling the bark with alcohol, precipitating the tannin (quercitannic acid) by gelatin, concentrating the filtrate, and recrystallising the quercitrin which separates from boiling alcohol. Quercitrin is most readily prepared by boiling the preparation of quercitron known as *flavin* with water, and cooling the filtered liquid. Quercitrin forms pale yellow, rhombic plates, which are odourless, have a somewhat bitter taste, and a feeble acid reaction. It is only slightly soluble in cold water or ether, more readily in boiling water (1 in 25), and easily in alcohol. Ammonia and the fixed alkalies dissolve quercitrin readily, with greenish-yellow colour. The ammoniacal solution rapidly oxidises, and turns brown on exposure to air. The aqueous solution of quercitrin gives a reddish-yellow precipitate with baryta water; a beautiful yellow colour with alum; flocculent yellow

Commercial Name.	Source.		Colouring Principle.	
	Botanical.	Geographical.	Name.	Formula.
Quercitron (page 339).	Bark of *Quercus nigra* or *Q. tinctoria*.	North America.	Quercitrin. Quercitin.	$C_{36}H_{38}O_{20}$ $C_{24}H_{16}O_{11}$
Old Fustic; Yellow Brazil wood (p. 343).	Wood of *Morus tinctoria*.	West Indies; South America.	Moric acid. Morintannic acid.	$C_{12}H_{10}O_6$ $C_{13}H_{10}O_6$
Young Fustic; Fustet wood (page 345).	Wood of *Rhus Cotinus*.	West Indies; Levant, South Europe.	Fustin or Fisetin.	$C_{23}H_{16}O_9$
Weld (page 347).	Leaves, &c., of *Reseda luteola*.	France, &c.	Luteolin.	$C_{20}H_{14}O_8$
Persian Berries; Yellow Berries (page 348).	Various species of *Rhamnus*.	Spain, France, Persia, Turkey, &c.	Xanthorhamnin.	$C_{48}H_{66}O_{27}$
Saffron (page 348).	Stigmata of flower of *Crocus sativus*.	Austria, Spain, France.	Crocin. Crocetin.	$C_{44}H_{70}O_{28}$ $C_{34}H_{46}O_9$
Annatto (page 352).	Pulpy parts of *Bixia Orellana*.	Mexico; South America.	Bixin.	$C_{28}H_{34}O_5$
Turmeric (page 357).	Underground stem of *Curcuma tinctoria*.	East Indies, China, Barbadoes.	Curcumin.	$C_{14}H_{14}O_4$
Gamboge (page 361).	Gum resin from *Garcinia morella*.	Siam, Cochin China, Ceylon.	Gambogin.	$C_{30}H_{35}O_6$

precipitates with the acetates of copper and lead; and an olive-green coloration and gradual precipitate with ferric sulphate. Nitric acid colours quercitrin orange-red.

Quercitrin is a glucoside, suffering hydrolysis when boiled with dilute sulphuric acid, with formation of quercitin and a sugar-like body. The formula of quercitrin is somewhat uncertain, and it is doubtful whether different observers have always worked on the same body. According to Hlasiwetz and Pfoundler, several kinds of quercitrin exist, all of which yield quercitin on treatment with dilute acids, but differ as to the kind of sugar simultaneously produced. But it seems more probable that quercitin and isodulcite are constant products of the hydrolysis, though the proportions formed depend on the origin of the glucose. Thus while rutin, $C_{24}H_{50}O_{25}$, contained in the leaves of *Ruta graveolens* and *Polygonum fagopyrum*, splits on hydrolysis into one molecule of quercitin and *one* of isodulcite, quercitin yields one of quercitin and *two* of isodulcite (vol. ii. 189), according to the following equation :—

$$\underset{\text{Quercitrin.}}{C_{36}H_{38}O_{20}} + 3H_2O = \underset{\text{Quercitin.}}{C_{24}H_{16}O_{11}} + \underset{\text{Isodulcite.}}{2C_6H_2O_5,H_2O}$$

Quercitin, $C_{24}H_{16}O_{11}$,[1] or its glucoside, is found in a great variety of plants. It forms slender needles of a bright yellow colour, which are tasteless, and insoluble in cold water. Quercitin is but slightly soluble even in hot water (1 in 280), but dissolves readily in alcohol and in acetic acid, and sparingly (1 in 125) in ether. In alkalies it dissolves with orange-yellow colour, and a crystalline compound, containing $C_{24}H_{16}O_{11},K_2O$, has been obtained by dissolving quercitin in a concentrated solution of potassium carbonate. An alkaline solution of quercitin becomes dark brown when treated with sodium-amalgam, the colour gradually changing to yellow. The alcoholic solution of quercitin yields orange precipitates with calcium, barium, and lead salts; gives an orange coloration with stannic chloride, and a green with ferric chloride.

Quercitin dissolves in strong sulphuric acid, apparently forming a sulphonic acid, and the solution dyes wool a fast yellow without a mordant. A di-acetyl-derivative has also been obtained.

If 1 part of quercitin be treated with 3 parts of caustic potash and 1 of water, and the whole evaporated to dryness, the quercitin is split up with formation of paradatiscetin, $C_{15}H_{10}O_6$, quercetic acid, $C_{15}H_{10}O_7$, and phloroglucol, $C_6H_6O_3$

---

[1] J. Herzig (*Jour. Chem. Soc.*, l. 251) has given reasons for doubting the accuracy of this formula.

(page 85). By prolonging the treatment with potash, or by treating quercetin at once with the fusing alkali, the quercetic acid is further decomposed into protocatechuic acid, $C_7H_6O_4$ (page 61), and quercimeric acid, $C_8H_6O_5$, which latter takes up oxygen and again splits up into protocatechuic acid and carbon dioxide.

Quercitin is easily decomposed when its acidulated aqueous solution is boiled.

When a dilute alcoholic solution of quercitin containing silver nitrate is shaken with three volumes of ether, the latter acquires a crimson colour rapidly fading with deposition of metallic silver.

If an alcoholic solution of quercitin be acidulated with hydrochloric acid and treated with sodium-amalgam, the liquid assumes a fine purple colour, and on concentration yields red prisms, which dissolve in alcohol and a little alkali with green colour, the solution being readily reoxidised with formation of quercitin on exposure to the air.

Besides quercitrin, quercitron bark contains quercitannic acid (page 93).

Flavin is the commercial name of a preparation of quercitron produced by acting on the bark with sulphuric acid, and hence contains woody fibre with more or less quercitrin, quercitin, and isodulcite. In some cases it consists of nearly pure quercitrin, and in others of quercitin. A good quality of flavin has about sixteen times the colouring power of quercitron bark, but very inferior specimens are sometimes met with. *Aurantine* and "patent bark" are preparations similar to flavin.

A freshly prepared decoction of quercitron bark is transparent, and of a dull orange-red colour, but after a time it becomes turbid, gives a yellow crystalline deposit, and the supernatant liquid gradually becomes gelatinous and acquires a blood-red colour. A freshly made solution is deepened in colour by alkalies and lime-water, the latter reagent also producing a brownish-yellow flocculent precipitate. Alum brightens the colour, and forms a light precipitate only. Stannous chloride gives a brown and stannic chloride a yellowish precipitate. Gelatin produces a reddish flocculent precipitate, and chlorine also precipitates abundant flocks, an excess of the reagent decolorising the liquid. Iron salts colour the solution of quercitron green, an olive-brown flocculent precipitate being subsequently formed.

Flavin and quercitron bark are chiefly used for dyeing woollen and mixed fabrics, tin being usually the mordant employed. Flavin is largely used in conjunction with cochineal or lac-dye for producing scarlet. Samples of flavin or quercitron are best assayed by a miniature dye-test.

Fibres dyed with quercitron bark yield a yellow solution with hydrochloric acid, but the colour of the fibre is little affected. Caustic alkalies behave similarly. Nitric acid turns the fibre light brown, and it becomes olive when boiled with ferric chloride, and orange with lead acetate. Alcohol has no action, and the colour is little affected by ammonia or an acid solution of stannous chloride, though the solution becomes yellow in each case.

OLD FUSTIC, also called *yellow wood* (page 340), contains two peculiar principles, known respectively as morin or moric acid, and morintannic acid or maclurin. To obtain these bodies in a pure state, rasped fustic is boiled with water and the decoction concentrated to a syrup. The crystalline deposit which forms in a few days is washed rapidly with cold water and pressed. On treatment with boiling water, morintannic acid is dissolved, while calcium morate remains insoluble. The morintannic acid is obtained by concentrating the solution, and crystallising the colouring matter from water acidulated with hydrochloric acid. The calcium morate is decomposed by dilute hydrochloric acid, and the residue taken up by alcohol, from which solution, on addition of two-thirds of its volume of water, the morin is deposited in yellow needles.[1]

Morin or *Moric Acid*, according to Benedikt and Hazura, probably contains $C_{13}H_8O_6$. It crystallises in colourless needles containing 1 *aqua*. It is nearly insoluble in water and carbon disulphide, slightly soluble in ether, and freely in alcohol. In solution of caustic alkalies, carbonates, borates, and phosphates, it dissolves with yellow colour, and is reprecipitated on addition of an acid. Ferric chloride gives an olive-green coloration with the alcoholic solution of moric acid, while yellow precipitates are produced by salts of tin, lead, zinc, and aluminium, and a dark green precipitate by cupric sulphate. If an alcoholic solution of moric acid be acidulated with hydrochloric acid and treated with sodium amalgam, it acquires an intense purple colour, and if then separated from the excess of the amalgam and concentrated, purple crystals are obtained of isomorin, a body said to be isomeric with morin.[2]

---

[1] Morin may also be prepared by mixing fustic extract with an equal volume of water and a little hydrochloric acid, decanting the clear liquid, and repeating the treatment till the washings are no longer yellow. The residue of crude morin is pressed, powdered, and dried in the air. It is then dissolved in hot alcohol, and one-tenth of hot water added, when free morin separates on cooling.

[2] Benedikt and Hazura (*Jour. Chem. Soc.*, xlvi. 1179) failed to obtain the isomorin of Hlaziwetz and Pfoundler.

The solution of this body becomes green on treatment with an alkali, and morin is gradually reproduced in the cold and rapidly on boiling. A solution of isomorin, when treated with alum, becomes intensely fluorescent, and on dilution appears yellow by transmitted and uranium-green by reflected light. The alcoholic solution of moric acid itself becomes highly fluorescent on addition of a minute proportion of alum (1 : 8000), a character which distinguishes it from morintannic acid, and has been suggested by Goppelsroeder as a delicate test for aluminium. When fused with caustic potash morin yields resorcinol, phloroglucol, and other products.

Moric acid presents a close analogy to quercitin (page 341) in many of its characters and reactions.

Morintannic Acid or *Maclurin*, $C_{18}H_{10}O_6+H_2O$ (page 79), forms a pale yellow, crystalline powder, freely soluble in water, and soluble also in alcohol, wood spirit, and ether. It becomes anhydrous at 130° and melts at 200° C. On boiling with concentrated caustic potash ley, or heating to 120° with dilute sulphuric acid, it splits up into protocatechuic acid and phloroglucol (compare page 84). With ferric chloride, morintannic acid yields a greenish or greenish-black precipitate. When boiled with hydrochloric acid it yields rufimoric acid, a substance forming brick-red crystals and dissolving in ammonia with purple coloration.

On heating a moderately concentrated solution of morintannic acid with zinc and diluted sulphuric acid, it rapidly acquires a red colour, which gradually changes to orange, and then contains phloroglucol (page 85) and machromin, $C_{14}H_{10}O_5$. The latter body crystallises in tufts of slender needles, only slightly soluble in water or alcohol, but more readily in ether. Both crystals and solutions of machromin become blue on exposure to air or treatment with oxidising agents. On adding hydrochloric acid the solution yields an amorphous blue precipitate, and with ferric or mercuric chloride a beautiful violet coloration, gradually changing to blue. In strong sulphuric acid, maclurin dissolves with orange colour, changing to intense green on heating. The colour is unchanged by dilution, but becomes purple on adding an alkali. The blue substance produced by the action of oxidising agents on machromin is said to contain $C_{14}H_8O_5$. It is best obtained by the employment of excess of ferric chloride, washing the blue precipitate which is formed, and after drying and washing it with ether. It dissolves in alcohol to form a solution which is decolorised by reducing agents.

A decoction of old fustic has a bitter, astringent taste. Alkalies and lime-water change the colour a reddish-brown. Acetic acid renders the decoction paler and brighter, and sulphuric, nitric, and oxalic acids produce slight precipitates. Chlorine-water produces a slight precipitate and reddish coloration, which is destroyed by excess. Alum gives a bright yellow precipitate with fustic decoction; stannous chloride, lead acetate, and gelatin yield golden or orange-yellow precipitates. Ferric sulphate produces an olive-brown coloration, and on standing a brownish-black precipitate falls.

Old fustic with an alumina mordant dyes wool yellow, and with salts of iron olive-green. Brighter colours can be obtained if the morintannic acid be first removed by gelatin. The yellows produced by fustic become orange on exposure to air and light, and hence it is now rarely employed alone; but when mordanted with potassium bichromate, it is largely used for the yellow constituent of browns, jet-blacks, and greens.

Fibres dyed with old fustic become orange on treatment with hydrochloric acid, and yield an orange solution. Nitric acid turns them pale yellow. By alkalies and ammonia the fibre is little changed in colour, though in the latter case the liquid is coloured yellow. An acid solution of stannous chloride changes the fibre to orange, the solution being colourless. Heated with ferric chloride, the colour of the fibre is changed to olive, and when boiled with aluminium acetate a yellow solution is obtained, exhibiting a bluish-green fluorescence.

Fustet Wood or Young Fustic (page 340), notwithstanding its name, is derived from quite a different source from old fustic. It occurs in commerce in small logs or crooked branches, that imported from the Antilles and the West Indies being the finest quality.

According to J. Schmidt (*Jour. Soc. Dyers, &c.*, ii. 148), fustet wood contains a substance which is easily broken up by the action either of dilute acids or alkalies into a kind of tannin (probably sumach-tannin) and the glucoside fustin. The red and brown colouring matters described by older investigators were probably oxidation-products or phlobaphenes of this tannin. The fustin-tannide may be prepared by treating young fustic with water, precipitating impurities by an acetic solution of lead acetate, and extracting the filtrate with acetic ether. It forms yellowish-white needles, easily soluble in water, alcohol, and ether. The solution gives with ammonia a brown, and with potash a brownish-red coloration, and reduces Fehling's solution. When dissolved in a little warm glacial acetic acid, and the solution diluted with water, yellowish-white needles of the glucoside fustin are obtained. This substance is readily soluble in boiling water, alcohol, and alkalies, but only sparingly in ether. With lead acetate it gives yellow and with cupric acetate a brownish-yellow precipitate, in both cases readily soluble in acetic acid. Ferric chloride gives a green coloration, changing through violet-blue to red on adding dilute soda. When warmed with dilute sulphuric acid, fustic is gradually decomposed into a sugar and fisetin.

Fisetin, $C_{23}H_{16}O_9$, may be obtained more readily from the commercial extract of fustet known as *colinin*, which is prepared by extracting the wood with very dilute caustic soda and evaporating the solution. Fisetin crystallises from dilute alcohol in small, lemon-yellow prisms. It is sparingly soluble in ether, benzene, petroleum spirit, chloroform, and boiling water, but readily in methyl and ethyl alcohols, and in ethyl acetate. Fisetin does not melt below 360°, but may be partially sublimed in small needles. Fuming sulphuric acid dissolves it with formation of a sulphonic acid. Alkalies and alkali-metal carbonates turn an alcoholic solution of fisetin brownish-red, and render it fluorescent. The absorption-spectrum is not characteristic. An alcoholic solution of fisetin gives a brilliant orange-red precipitate with lead acetate, an orange yellow with stannous chloride, and a brown precipitate with cupric acetate. The precipitates in each case are readily soluble in acetic acid. Fisetin reduces Fehling's solution and ammoniacal silver nitrate on warming. If an alcoholic solution of fisetin be acidified with sulphuric acid and treated on the water-bath with sodium-amalgam, the liquid acquires a beautiful purple-red colour.

When heated with glacial acetic acid and sodium acetate, fisetin yields a hexacetyl-fisetin, $C_{23}H_{10}(C_2H_3O)_3O_9$, which crystallises in white needles sparingly soluble in boiling alcohol, readily in chloroform, and melting at 200° to 201° C.

When fisetin is dissolved in a warm saturated solution of sodium carbonate, a sodium derivative, $C_{23}H_{14}Na_2O_9$, crystallises out in yellow glistening needles, which turn greenish-black on exposure to air. When fused with caustic potash, fisetin yields phloroglucol and protocatechuic acid (page 84).

Fisetin presents a close resemblance to quercitin, from which, if the formula of Liebermann and Hamburger for the latter be correct, it only differs by CO_2.[1]

A decoction of young fustic gives a fine orange colour with alkalies, and bright orange precipitates with lime and baryta water, stannous chloride, and lead acetate. Acids give it a greenish hue. Ferric sulphate produces an olive-green, and cupric acetate a dark red precipitate.

---

[1] According to Hlaziwetz and Pfoundler, the formula of quercitin is $C_{27}H_{18}O_{12}$ (compare page 341).

Young fustic gives a fine orange colour with alumina mordants, and is employed in conjunction with cochineal and lac-dye in dyeing scarlet, the mordants being tartar and stannous chloride. It is also used for dyeing leather orange-yellow. The colours are not so fast as many vegetable yellows and oranges.

On the fibre, colours dyed with young fustic are unchanged by hydrochloric acid, the solution becoming pale yellow. Soda and ammonia turn the fibre reddish-brown, and nitric acid dark brown. Alcohol and an acid solution of stannous chloride have no action. Heated with ferric chloride the fibre becomes olive.

Weld (page 340) consists of the leaves and other parts of a variety of mignonette. *Luteolin*, the colouring matter of weld, probably has the formula $C_{20}H_{14}O_8$, and forms small yellow needles having an astringent, bitter taste. It dissolves slightly in cold and very sparingly in boiling water, but is more soluble in alcohol. It dissolves readily in alkalies with deep yellow colour, and in cold sulphuric acid to form a reddish-yellow solution precipitated on dilution with water. Ferric chloride employed in small proportion produces a green coloration, which changes to brownish-red on adding excess of the reagent. Oxidising agents, such as potassium bichromate, turn luteolin a brilliant yellow. On fusion with potash, luteolin yields hydrogen, protocatechuic acid, and much phloroglucol.

A decoction of weld is pale yellow when freshly prepared, but soon becomes turbid, and gives a greenish-brown precipitate containing iron. It is slightly acid, and turns reddish when kept. Alkalies change the colour to a golden yellow, and baryta water precipitates beautiful yellow flocks. Alum gives only a slight yellow precipitate, but lead acetate and stannous chloride produce abundant yellow precipitates. Gelatin only renders the liquid slightly turbid, while ferric sulphate gives an olive-brown coloration, and, on standing, a brown precipitate. Chlorine changes the colour of a decoction of weld to brown, and gives a flocculent precipitate; an excess of the reagent partially decolorises the liquid. Potassium bichromate changes the colour to golden yellow, and then gives a precipitate in yellow plates. Most acids render the liquid turbid, but nitric acid deepens the colour, without producing any precipitate.

An aqueous solution of weld dyes wool, mordanted with alum, a fine daffodil-yellow, which is very fast to light, heat, and dilute acids.

On the fibre, colours dyed with weld are little affected by hydrochloric acid, though the solution is turned pale yellow. Ammonia, alcohol, nitric acid, boiling lead acetate, and an acid solution of stannous chloride have little or no visible action. With caustic soda the fibre is but little affected, but the solution becomes pale yellow.

PERSIAN or YELLOW BERRIES are the fruit of the buckthorn and other species of *Rhamnus* (page 340) growing in the east and the south of Europe. They are about the size of peas, shrivelled, and yellowish-green in colour. When old or injured they are brown or black. The flavour of yellow berries is bitter and disagreeable, and the odour unpleasant.

Xanthorhamnin or *Chrysorhamnin*, the yellow colouring matter of Persian berries, has, according to Liebermann and Hörmann, the formula $C_{48}H_{66}O_{29}$. It forms golden yellow crystals, and, when boiled with dilute sulphuric acid, or even when simply heated to 130°–160° C., it is hydrolysed into rhamnetin and the saccharoid body iso-dulcitol (vol. i. page 189). The following formula expresses the decomposition which is stated to occur:—

$$\underset{\text{Xanthorhamnin.}}{C_{48}H_{66}O_{29}} + 5H_2O = \underset{\text{Rhamnetin.}}{2C_{12}H_{10}O_5} + \underset{\text{Iso-dulcitol.}}{4C_6H_{14}O_6}$$

Rhamnetin crystallises from water containing sulphuric acid in microscopic needles, and from phenol in distinct yellow needles.

A freshly prepared decoction of yellow berries has a brownish-green colour. It is very liable to ferment and become ropy, but the change may be prevented by addition of carbolic acid. The solution is brightened or rendered slightly turbid by acids, while alkalies change the colour to orange. Alum weakens the colour without forming a precipitate, and chlorine deepens it to red, or with excess changes it to yellow. Acetate of lead renders the decoction of yellow berries turbid after a time, and other metallic solutions fail to produce characteristic changes.

Persian berries give bright yellows on wool and cotton with alumina or tin mordants. Their use has much diminished.

SAFFRON consists of the stigmata of the flowers of *Crocus sativus* (page 340), of which from 50,000 to 100,000 are required to produce 1 lb. weight. It has an agreeable odour, and a bitter pungent taste.

The chemistry of saffron has been recently re-investigated by R. Kayser (*Jour. Soc. Dyers, &c.*, i. 43). The essential oil is obtained by distilling saffron with water in a current of carbon dioxide, agitating the distillate with ether, and evaporating the ether in an atmosphere of carbon dioxide. It is a very mobile, nearly colourless liquid of the terpene class, $C_{10}H_{16}$, having an intense odour of saffron, and very prone to absorb oxygen and become thick and brown.

If saffron be treated with ether, to remove the fat and essential oil, and the residue treated with cold water, the colouring matter is dissolved. On shaking this solution with purified animal charcoal the colour is rapidly absorbed, and on filtering and boiling the charcoal with rectified spirit, it again passes into solution. The filtered liquid yields crocin on evaporation.

Crocin, so obtained, according to R. Kayser has the formula $C_{44}H_{70}O_{28}$. It forms a yellowish-brown mass, the powder of which is yellow. It dissolves readily in water and dilute alcohol, but with difficulty in absolute alcohol or ether. Concentrated sulphuric acid dissolves it with blue colour, changing to violet, cherry-red, and finally to brown. Concentrated nitric acid also gives a blue coloration, changing to brown, but hydrochloric acid dissolves crocin without alteration.

By the action of hot lime or baryta water, or even hot acetate of lead solution, crocetin is hydrolysed with formation of a glucose, crystallising in rhombs, and a body called crocetin, $C_{34}H_{46}O_9$. The latter is best prepared by heating crocin with dilute hydrochloric acid in a current of carbon dioxide, when crocetin is precipitated as a red powder, scarcely soluble in water, but soluble in presence of an alkali with orange colour, and reprecipitated on adding an acid.

Picrocrocin, $C_{38}H_{66}O_{17}$, is obtained in bitter prismatic crystals, melting at 75°, and soluble in water and alcohol, on extracting dried saffron with ether for a prolonged time. When warmed in aqueous solution with a dilute acid, lime or baryta water, or lead acetate, picrocrocin splits up into a sugar and the terpene of a saffron-odour already described.

Saffron is too expensive to use in dyeing, but is employed for colouring pastry, and has a limited use in medicine. It is liable to various substitutions and adulterations, which are classified by J. M. Maisch (*Analyst*, x. 200) as those derived from the same plant and those coming from other sources. The stigmata of which genuine saffron consists become thinner towards the leaves, *terminate in a yellow thread*, and three are generally united. Saffron *styles* are present in all saffron of Spanish origin to a greater or less extent, and crocus *stamens*, dyed so as to resemble the stigmata, are also met with. Fibres of shredded *beef* and *ham* are said to be a common adulterant in Italy. Such an addition would be readily detected by the microscope, and the smell produced on heating will afford a preliminary indication of their presence. The *corolla tubes* of the crocus, dyed with brazil-wood or santal-wood, are said to be frequently used for adulterating saffron. Various other coloured vegetable products are referred to by Maisch, including the *calendula* florets (marigold) dyed by *dinitrocresylate of sodium* observed by J. Biel. This fraud may be detected by treating the suspected portions of the sample with petroleum ether, which is not coloured by genuine saffron, but dissolves the coal-tar colour with citron-yellow colour. The colouring matter from *santal-wood* is not taken up by water, but dissolves in alcohol with red and in ammonia with purple-red colour. Brazil-wood will tinge the water red in a few minutes, the colour becoming pale on adding acid and deeper with ammonia, but the infusion will not be blackened by salts of iron.

Safflower and *red poppy* have also been observed as adulterants of saffron. In the latter case the infusion is turned greyish-green by ammonia, and bright red by nitric acid. Safflower is said to be so commonly substituted for saffron in some parts of America that the genuine substance is unknown (*Pharm. Jour.*, [3], vi. 950).

Mineral additions, such as chalk, gypsum, barium and sodium sulphate, emery, &c., have been observed as adulterants of saffron, being made to adhere by means of honey, glucose, or glycerin. The ash of genuine saffron of good quality ranges from 4 to 7 per cent., but in samples of Alicante saffron D. Hanbury (*Pharm. Jour.*, [3], i. 241) found proportions of ash varying from 12 to 28 per cent., the excess being due to mineral adulterants. J. Ingham has described a sample of saffron containing 45 per cent. of mineral impurity, besides a quantity of crocus stamens; J. Hart a saffron yielding 20 per cent. of ash, the greater part of which consisted of barium sulphate; and Tanner a sample containing a considerable quantity of a red ferruginous earth. M. Adrian has described a saffron yielding 26·4 per cent. of ash, containing borate, chloride, sulphate of sodium, and carbonate of potassium, the last having probably been derived from tartrates. The presence of ammonium nitrate was also suspected. E. M. Holmes (*Pharm. Jour.*, [3], xix. 666) met with an adulterated saffron of excellent odour and colour, which immediately coloured water orange-yellow, deflagrated like touch-paper on ignition, gave a fusible ash, and yielded the brown coloration indicative of a nitrate with ferrous sulphate and sulphuric acid.

Grispo found vegetable filaments of unknown origin in saffron, together with water, glucose, and barium sulphate. Kanoldt examined a factitious saffron that consisted entirely of an alga, probably *Fucus amylaceus*, which had been weighted with a coloured mixture of chalk and honey.

For the detection of mineral adulterants in saffron, D. Hanbury recommends that about 1 grain of the sample should be treated on a watch-glass with 8 or 10 drops of water, and then lightly touched so as to cause the water to wet it. Genuine saffron will yield immediately a *clear* bright yellow solution, but if a mineral adulterant be present a white powder will *instantly separate*, and will render the liquid turbid; and on adding hydrochloric acid a perceptible effervescence and disappearance of the turbidity will be observed if a carbonate be present, whereas the pollen from crocus stamens is unaffected, and its nature can be recognised under the microscope. If it be desired to collect the adulterant, the saffron should be stirred with water in a funnel closed at the lower end. The mineral matter will settle into the stem, and after removing the saffron and pouring off the bulk of the water, can readily be washed out and further examined.

If genuine saffron be scattered on the surface of warm water, it immediately expands into a characteristic form, readily distinguished from crocus stamens, or the florets of safflower, marigold, or arnica.

According to the *German Pharmacopœia*, "if 1 part of saffron be macerated in 10 parts of water, a yellow-red liquid is obtained free from sweet taste, and which, diluted with 10,000 parts of water, has a distinct yellow colour. Saffron on being dried at 100° C. should lose less than 14 per cent. of moisture, and on being now incinerated should leave not more than 8 per cent. of ash." From this description it appears that 1 grain of saffron will colour 7 gallons of water distinctly yellow.

B. S. Proctor (*Pharm. Jour.*, [3], xix. 801) states that saffron is best assayed, in the absence of other colouring matters, by comparing the colour of the infusion with that of a solution of potassium bichromate. 1·4 grammes of this salt, dissolved in 100 c.c. of water, is said to furnish a liquid of the same tint as that produced by exhausting 0·1 gramme of genuine saffron by several alternate treatments with methylated spirit and water, and diluting the mixed decoctions to 100 c.c. These solutions are too strong for the accurate observation of the colour, and hence should be further largely diluted before comparing the tints. 1 c.c. of the bichromate solution should be measured with a delicate pipette, and diluted with 50 c.c. of water. To a similar quantity of water, in another tube, sufficient of the saffron infusion is gradually added from a graduated pipette to render the colour similar to that of the bichromate solution.

Saffron gives a fine yellow colour on silk, but is now rarely if ever used as a dye. It is employed in medicine, and would probably be more extensively applied if the price were lower.

Annatto, occasionally called *arnotta* and *rocou* (page 340), is mainly composed of the pulp surrounding the fruit of *Bixa orellana*, growing in the East and West Indies and South America. The two chief kinds which reach England are Spanish annatto, imported from Brazil, and the flag or French annatto which comes from Cayenne. Brazil annatto occurs in cakes or rolls, is hard and dry, brownish on the exterior but red inside, and with a rather agreeable odour. Cayenne annatto is a soft paste, of a bright yellow colour. It often has a repulsive urinous odour, said to be due to the actual addition of urine to keep it moist and impart a richer colour.

Annatto contains two yellow colouring matters, bixin and orellin.

Bixin, $C_{28}H_{34}O_5$, the properties and chemical relationships of which have been very imperfectly examined, may be prepared by digesting annatto at about 80° C. with rectified spirit and sodium carbonate. The filtered liquid is treated with half its measure of water and a saturated solution of sodium carbonate. The precipitate, consisting of the sodium salt of bixin, is purified by re-solution in weak alcohol and precipitation by sodium carbonate, and is then decomposed by hydrochloric acid. Bixin forms minute yellow leaflets which melt at 176°. It is insoluble in water, and only slightly soluble in alcohol, benzene, carbon disulphide, or acetic acid, but is very readily soluble in ether.[1] Bixin forms a sodium salt, containing $C_{28}H_{33}NaO_5$, 2 *aqua*, which crystallises in lustrous red needles, very soluble in water, but insoluble in alcohol and ether. It also yields a compound containing $C_{28}H_{32}Na_2O_5$, 2 *aqua*, which forms a dull red powder.

According to some observers, bixin reduces Fehling's solution even in the cold, but according to others it has no action even after boiling with dilute sulphuric acid. It dissolves in strong sulphuric acid with bright blue colour, and on dilution with water a dark green precipitate is formed.

Orellin is described as yellow, soluble in water and alcohol, but insoluble in ether, and dyeing cloth mordanted with alum yellow. It is probably an oxidation-product of bixin.

Annatto is only partially soluble in water, but more completely in alcohol. It dissolves readily but sometimes imperfectly in solutions of caustic and carbonated alkalies, of borax, and of soap, forming liquids of orange or red colour, which furnish orange-red precipitates with acids. It gives orange lakes with alumina and ferrous sulphate, a yellowish-brown precipitate with salts of copper, and a lemon-yellow with tin salts. Concentrated sulphuric acid dissolves annatto with deep blue colour, the colour gradually changing to green and violet. On adding water a deep green precipitate is formed.

---

[1] According to some authorities, bixin is insoluble in ether, but readily soluble in alcohol.

Commercial annatto varies greatly in quality, and is liable to various adulterations. According to Wynter Blyth, a fair commercial sample contained:—water, 24·2; resin, 28·8; ash, 22·5; and extractive matters, 24·5 per cent. An adulterated sample contained:—water, 13·4; resin, 11·0; ash (oxide of iron, alumina, silica, chalk, and common salt), 48·3; and extractive matters, 27·3 per cent. Crace-Calvert gives the average composition of inferior Cayenne annatto as:—water, 72·25; leaves, 3·85; starch, mucilage, and woody fibre, 18·30; and, colouring matter, 5·60 per cent.

The following results, obtained by the analysis of commercial annatto, have been recorded by W. Lawson (*Pharm. Jour.*, [3], xvi. 645).

No. of Sample.	Moisture.	Resin.	Extractive.	Total Ash.	Soluble Ash.	Remarks.
1	21·75	3·00	57·29	17·96	13·20	Red roll. Ash was largely NaCl.
2	21·60	2·90	59·33	16·17	12·57	Red roll. Ash was largely NaCl.
3	20·39	1·00	65·00	13·61	7·50	Red roll. Ash large, chiefly NaCl and Fe_2O_3.
4	69·73	8·80	19·47	2·00	...	Bright red paste. Ash chiefly NaCl.
5	18·00	3·00	58·40	20·60	10·00	Red roll. 3 per cent. of sand.
6	18·28	1·80	65·67	14·25	11·75	Red roll. Contained iron and foreign matters.
7	15·71	5·40	26·89	52·00	18·50	Brown cake. Soluble ash chiefly K_2CO_3, and insoluble $CaCO_3$.
8	38·18	1·20	20·82	29·00	20·00	Brown cake. Very offensive. Soluble ash chiefly K_2CO_3.
9	19·33	5·99	23·77	51·00	15·00	Brown cake. Resembled No. 7.
10	29·50	9·20	28·50	39·80	13·80	Brown cake. Resembled No. 7.

The *resin* was determined by drying the samples at 100° (the loss of weight being recorded as *moisture*), and then exhausting with boiling methylated spirit. The alcoholic solution was evaporated on the water-bath, the residue dissolved in carbonate of sodium, and the solution precipitated by a very slight excess of dilute sulphuric acid. The precipitated resin was filtered off, washed, dried, and weighed. The *ash* was determined by ignition, and the *extractive matter* by difference.

The samples in the form of brown cakes gave on ignition an agreeable odour resembling that of good tobacco. Most of the red rolls contained abundance of starchy matters, this in No. 4 being largely replaced by water. The cakes all gave the boric acid reaction for turmeric, and all except No. 8 contained large quantities of chalk.

Besides containing the adulterants already mentioned, annatto is liable to be mixed with ochre, brick-dust, &c.

The colouring power of annatto is best ascertained by a dye-assay in a bath containing soap or sodium carbonate.

Annatto receives a limited application in dyeing and calico-printing, but by far the greater part is employed for colouring butter and cheese.

Butter colourings are now numerous. Among the substances employed for the purpose, E. Schmidt (*Jour. Chem. Soc.*, xlvi. 286) enumerates marigold and carthamus flowers, saffron(?), carrot juice, and turmeric. More recently the coal-tar colours known as coralline yellow and victoria yellow are said to have been used, as also dimethyl-amido-azobenzene (page 180). Lead chromate has been met with as a colour on the outside of cheese.

Various methods have been described for the recognition of butter-colourings, the process being usually based on the solution of the butter-fat in ether or similar solvents, the agitation of this liquid with alkali, the precipitation of the dissolved colouring matter by an acid, and the application of special tests to the precipitate.

To extract *naphthalene-yellow* from butter, the fat should be separated from the curd, water, &c., dissolved in ether, and the solution agitated with water, to which dilute ammonia is added drop by drop until present in slight excess. The naphthalene yellow or other added colouring matter, *e.g.*, annatto, turmeric, saffron, &c., will dissolve in the ammoniacal liquid. *Turmeric* will be indicated by the formation of a brownish or reddish stratum between the ethereal and aqueous layers before they are thoroughly mixed by agitation.

E. W. Martin (*Analyst*, xii. 70) recommends that 2 parts of carbon disulphide should be gradually added, with gentle agitation, to 15 parts of alcohol or wood spirit. Five grammes of the butter to be tested, which need not be previously clarified, is shaken with 25 c.c. of the solution so obtained. On standing for a few minutes, the mixture separates into two layers, the lower of which is a solution of the fat in carbon disulphide, while the upper alcoholic stratum will be yellow if any artificial colouring matter be present. If the butter be but slightly coloured, a larger amount should be employed. The alcoholic stratum will give a greenish coloration with nitric acid, and a red with hydrochloric acid and sugar if *saffron* be present. A brownish colour with ammonia indicates *turmeric*, and a blackish coloration with silver nitrate, *marigold*. If the alcoholic solution be evaporated to dryness, and the residue treated with concentrated sulphuric acid, *annatto* will be indicated by a greenish-blue, and *saffron* by a blue coloration. On adding a few drops of boric acid solution (or a solution of borax to which sufficient hydrochloric acid has been added to distinctly redden litmus), and again evaporating, *turmeric* will be indicated by a bright brownish-red coloration, changed to blue, green, or violet by caustic alkalies. *Dinitro-cresol* and *dinitro-naphthol* will be detected by treating the residue with ammonia, and adding excess of hydrochloric acid, when a light yellow crystalline precipitate will be formed, soluble in ether. The residue obtained, on evaporating the ethereal solution, is soluble in alcohol, and after dilution with water the hot solution will dye a fibre of silk or wool yellow without a mordant.

R. W. Moore has pointed out (*Analyst*, xi. 163) that, when a butter coloured with *carotin* is dissolved in carbon disulphide and shaken with alcohol, as prescribed by Martin, the alcohol remains colourless, while the lower layer is deeply coloured; but on adding a drop of a dilute solution of ferric chloride and again shaking, a gradual change is observed, the alcoholic layer becoming distinctly yellow and the bisulphide solution of the fats quite colourless, or retaining only the pale yellow colour due to the natural colouring matter of the butter. Excess of ferric chloride must be avoided.

A. R. Leeds (*Analyst*, xii. 150) has described a general method for the detection of butter-colourings. He recommends that 100 grammes of the butter should be dissolved in a tapped separator in 300 c.c. of petroleum ether of about 0·638 specific gravity. The water, &c., are tapped off, and ethereal solution of the fat and colouring matters washed several times by agitation with water. The ethereal solution, poured off from any stearin which may have separated on standing, is then shaken with 50 c.c. of a decinormal solution of caustic potash (5·61 grammes of KHO per litre), which is usually sufficient to effect the solution of all colouring matters capable of being dissolved by dilute alkali.[1] The alkaline solution is separated from the ethereal layer, and very cautiously treated with dilute hydrochloric acid until faintly acid to litmus paper. The precipitate, consisting of colouring matter mixed with a little fatty acid, is filtered off and washed with cold water. If desired, it may be weighed.

The following table shows the reactions of the colouring matters, isolated in the above manner, when two or three drops of their alcoholic solutions were treated with an equal measure of the reagents (acids) mentioned.

---

[1] Even after agitation with caustic alkali the petroleum ether always retains a pale yellow colour, which is not removed or lessened by repeating the treatment with alkali. This is due to the natural or yellowish colour of the butter fat itself, and not to any added colouring matters. It may be destroyed without any sensible change to the butter fat.

Colouring Matters.	Reaction with			
	Concentrated Sulphuric Acid.	Concentrated Nitric Acid.	Mixed Sulphuric and Nitric Acids.	Concentrated Hydrochloric Acid.
Annatto.	Indigo - blue, changing to violet.	Blue, becoming colourless on standing.	Blue, becoming colourless on standing.	No change, or merely dirty yellow or brown colour.
Annatto with decolorised butter.	Blue, becoming green, and slowly changing to violet.	Blue, becoming green and colourless.	Decolorised.	No change, or only dirty yellow.
Turmeric.	Rose-violet.	Violet.	Violet.	Violet, becoming yellow on evaporation of the acid.
Turmeric with decolorised butter.	Violet, changing to purple.	Violet to reddish-violet.	Violet to reddish-violet.	Very fine violet.
Saffron.	Violet to cobalt blue, changing to reddish-brown.	Light blue, changing to light reddish-brown.	Light blue, changing to light reddish-brown.	Yellow, changing to dirty yellow.
Saffron with decolorised butter.	Dark blue, rapidly changing to reddish-brown.	Blue, changing to green and brown.	Blue, rapidly changing to purple.	Yellow, becoming dirty yellow.
Carrot.	Amber brown.	Decolorised.	Decolorised, with red fumes and odour of burnt sugar.	No change.
Carrot with decolorised butter.	Reddish-brown to purple.	Yellow and decolorised.	Yellow and decolorised.	Slightly brown.
Marigold.	Dark olive green, not changing in colour.	Blue, instantly changing to a dirty yellowish-green.	Green.	Green to yellowish-green.
Safflower.	Light brown.	Partially decolorised.	Decolorised.	No change.
Aniline yellow.	Yellow.	Yellow.	Yellow.	Yellow.
Martius' yellow.	Pale yellow.	Yellow - red precipitate; magenta at margin.	Yellow.	Yellow precipitate, which deflagrates when treated with ammonia and heated.
Victoria yellow.	Partially decolorised.	Partially decolorised.	Partially decolorised.	Yellow colour returns on neutralising with ammonia.

The butter-colouring sold as "carottine" is apparently a solution of 1 part of annatto in 4 parts of oil, the annatto being partially replaced by turmeric for the lighter shades. "Orantia" is a solution of annatto and carbonate of sodium in water.

Carotin, the colouring matter contained in the root of the carrot (*Daucus carota*), may be prepared by exhausting the finely-divided root with water, precipitating the solution with tannin and a little sulphuric acid, and exhausting the washed precipitate with boiling alcohol at 80 per cent. This takes up mannitol, $C_6H_{14}O_6$, and hydrocarotin, a body closely resembling cholesterin. The residue insoluble in alcohol is treated with carbon disulphide, the resultant solution evaporated, and the residue treated with absolute alcohol. The solution obtained yields, on concentration, a precipitate of carotin as a brownish-red crystalline substance with a metallic reflection. Pure carotin forms rhombic leaflets, which appear blue in reflected and red-orange in transmitted light. It is soluble in benzene and carbon disulphide, but insoluble in water or hydrous alcohol. Carotin is decolorised by heat or exposure to light. It dissolves in sulphuric acid with indigo-blue or violet colour, while sulphurous acid also colours it indigo-blue. With iodine it yields a derivative of deep green colour and metallic lustre.

Husemann attributed to carotin the formula $C_{18}H_{24}O$, but according to Arnaud this was probably an oxidised product, the pure substance being an unsaturated hydrocarbon of the formula, $C_{28}H_{28}$, which he proposed to call carotene. This latter formula is probably incorrect, as no other coloured hydrocarbon is known.

Carotin appears to be a constant and normal product of vegetable life, and to be frequently present in the leaves of the most vigorous plants, and consequently those that are the most intensely green, its presence in such cases being masked by the green colour of the chlorophyll. It may be detected and approximately estimated by carefully drying the leaves in a vacuum over sulphuric acid, digesting in the cold for ten days with petroleum spirit, evaporating to dryness in an open dish, and dissolving the residue in a little carbon disulphide. The resultant solution is intensely red, and is examined colorimetrically against a standard solution of pure crystallised carotin, containing 0·010 gramme per litre. The proportion of carotin in dry leaves often approaches 0·1 per cent. (M. A. Arnaud, *Jour. Soc. Dyers, &c.*, iii. 99).

TURMERIC or **INDIAN SAFFRON** (page 341) is the tuber or underground stem of *Curcuma tinctoria* or *longa* and *C. rotunda.* The colour of the roots externally is generally greyish, but in the interior they are usually a deep yellow.[1]

---

[1] The principal commercial varieties of turmeric are:—*Chinese*, consisting of many central rhizomes with well-developed branches; *Bengal*, mostly in slender branches of a deep reddish tint; *Java*, which consists of rather small tubers and branches that are often transversely and longitudinally cut; and *Cochin turmeric*, in sections or slices of a larger tuber, some being marked with rather large depressed stem-scars.

According to John, turmeric-root contains:—yellowish volatile oil, 1; yellowish-brown resin, 10 to 11; brown extractive matter, with dyeing properties, 11 to 12; gummy matter, 14; matter soluble in alkalies, including earthy salts, 57; and moisture, loss, &c., 7 to 5 per cent. The presence of starch is not indicated in this analysis, though turmeric-root contains a sufficient proportion for iodine solution to change the whole colour from yellow to blue.

The powder of turmeric has a strong odour and a very bright orange colour. The taste is bitter and aromatic. Cold water dissolves but little colouring matter, but boiling water extracts a larger quantity. Alcohol dissolves the colouring matter freely, and likewise takes up the greater part of the resin.

Curcumin, $C_{14}H_{14}O_4$, is prepared by F. W. Daube by steaming powdered turmeric to remove the volatile oil, washing with boiling water till the washings are no longer coloured, drying, and extracting the residue with a large quantity of boiling benzene. The solution is evaporated to the crystallising point, the crystals dissolved in spirit, the solution precipitated with basic lead acetate, and the lead compound decomposed by sulphuretted hydrogen. The product is recrystallised from boiling alcohol. Another method is to exhaust ground turmeric with carbon disulphide to remove the volatile oil and resinous matters, and treat the residue with weak caustic alkali. On neutralising the alkaline solution with an acid, the curcumin is precipitated, and after drying may be recrystallised from ether.

According to Jackson and Menke (*Amer. Chem. Jour.*, iv. 77, and *Jour. Chem. Soc.*, xlii. 1107) curcumin may be obtained pure by treating ground turmeric-root with petroleum spirit to remove the volatile oil, and then with ether, which dissolves the curcumin together with a large quantity of resin. The product is purified by crystallisation from alcohol. Thus prepared, curcumin crystallises from hot alcohol in stout needles or shining prisms, which have an orange or red colour and a beautiful blue reflection. Curcumin is odourless when pure, melts at 178° C., and is only slightly soluble in water, even when boiling. It is difficultly soluble in cold but more readily in boiling alcohol, and is also soluble in ether, the solution exhibiting a strong green fluorescence. It is also soluble in wood spirit and glacial acetic acid, but only slightly so in benzene or carbon disulphide, and is all but insoluble in petroleum spirit. Strong sulphuric acid dissolves curcumin with fine reddish-purple colour, gradually changing to black from charring, and the same effect is produced, though more slowly, by strong hydrochloric acid.

Curcumin dissolves readily with reddish-brown colour in solutions of caustic and carbonated alkalies, and to a slight extent when boiled with water and calcium carbonate. The ammoniacal solution gives off ammonia when boiled, and deposits curcumin. On adding a large excess of strong alcoholic potash to a hot alcoholic solution of curcumin, the potassium salt, $C_{14}H_{12}K_2O_4$, separates in globular radiated groups of flame-coloured crystals, which assume a claret colour when dried. The precipitation may be made more perfect by adding ether, in which the new compound is nearly insoluble, though soluble in alcohol and freely so in water. On exposure to air, the alcoholic solution of potassium curcumate assumes a magenta colour, probably from oxidation. When excess of potassium carbonate is added to a hot solution of curcumin in absolute alcohol, the acid salt, $C_{14}H_{13}KO_4$, is formed, and on adding ether separates in crimson-black flocks resembling magenta. The solution gives coloured precipitates with metallic salts.

By treatment with chromic acid mixture curcumin is completely oxidised to acetic and carbonic acids, without any terephthalic acid (page 47) being formed. By oxidation with permanganate in alkaline solution it yields vanillin (page 62).

In consequence of the sensitiveness of curcumin to alkalies, turmeric is sometimes used as an indicator of alkalinity. The yellow colour is restored by very weak acids, and hence turmeric has been proposed for titrating fatty acids, for which purpose, however, phenol-phthaleïn is better adapted (see vol. ii. 76; and R. T. Thomson, *Jour. Soc. Chem. Ind.*, vi. 195). The alcoholic solution of turmeric exhibits a well-marked fluorescence.

The most characteristic reaction of curcumin and turmeric is that with boric acid. If an alcoholic solution of turmeric or curcumin be mixed with one of boric acid, it becomes of deep red colour, distinct from that produced by alkalies. A convenient way of applying the test is to place a small disk of filter-paper, about 1 inch in diameter, in the turmeric tincture, and evaporate the latter to dryness at 100°. On the paper is then poured an aqueous solution of boric acid, or a solution of borax to which sufficient hydrochloric acid has been added to render it distinctly acid to litmus. The red colour will probably be at once developed, but if not will become apparent on evaporating the liquid to dryness. On now adding a drop of caustic alkali, a very beautiful series of colours will be produced, green and purple being the most prominent. On adding hydrochloric acid a red colour is produced, which is again turned green and blue on addition of excess of alkali.[1]

---

[1] In 1874, the author recommended this mode of operating to effect the detection of turmeric in mustard (*Chem. News*, xxx. 116).

The reaction of curcumin with boric acid appears to be due to the formation of a substance called by Schlumberger rosocyanin, which may be prepared by treating an alcoholic solution of curcumin with boric and sulphuric acids. The liquid acquires a deep red colour, which changes gradually in the cold, and rapidly on heating, to dark red, orange, and finally to yellow. Hence the operation should be arrested when a sample is found to become blue on adding ammonia. The impure rosocyanin crystallises out as the solution cools. When pure, it forms dark red needles with a green reflection, and is insoluble in water, ether, or benzene. The alcoholic solution has an intense rose-red colour, but rapidly changes. It is turned blue by ammonia, the original colour returning on adding an acid. The alkaline solution becomes grey on exposure to air, and gives blue precipitates with lime or baryta water.

Turmeric is not employed alone as a dye for fabrics (except in China), but is used to some extent in certain mixed colours known as "sour browns." It is one of the few colouring matters for which cotton has a strong attraction. Cotton may be dyed without a mordant by heating in a bath of turmeric at 60°. Turmeric is also employed in paper-staining, and for dyeing wood and leather; also as a colouring for butter, cheese, pastry, &c. It is an important ingredient of curry powder.

Powdered turmeric is sometimes adulterated with starch and mineral matters. The *ash* should not exceed 5 to 6 per cent. Common salt is added to turmeric to give it a brighter appearance, but interferes with some of its uses. Turmeric should be quite dry. If damp it becomes yellowish-brown, and is rendered unfit for its chief applications. The characteristics of good turmeric are a rich, deep, but bright, orange colour, and a strong aromatic, rather pungent odour. Turmeric may be assayed by dyeing equal weights of white woollen cloth at 60° C. with solutions of equal weights of the samples, using no mordant. The dyed pieces are examined for depth of colour, and also held horizontally in front of a window and viewed along the surface. In this position cloth dyed with good turmeric shows a beautiful golden lustre, on the purity of which its value for many purposes depends, as for the yellow cotton warps of figured table-covers.

On the fibre, turmeric is turned reddish-brown by hydrochloric acid, or an acid solution of stannous chloride, without the solution becoming coloured. Caustic soda and ammonia turn the fibre bright reddish-brown, the solution becoming brownish-orange. Alcohol extracts the colour, producing an orange or yellow solution with green fluorescence. Nitric acid turns the fibre pale yellow.

Gamboge (page 340) is a gum-resin produced by trees growing in various parts of the Malay peninsula. It occurs in cylindrical, hollow, or solid rolls,[1] longitudinally striated on the surface, and either distinct or more or less agglutinated or folded together in masses. Externally it is brownish-yellow, and is covered with a yellow powder. When broken it exhibits a vitreous or conchoidal fracture, the fractured surface being opaque, smooth, glistening, and of a uniform reddish-yellow colour. The powder is bright yellow, and forms a yellow emulsion with water. Although nearly without odour at the ordinary temperature, gamboge evolves a very peculiar smell when heated. The taste is at first scarcely perceptible, but after a time it produces a sharp acrid sensation in the throat. Gamboge acts as a drastic purgative, and is the active constituent of a well-known patent pill.

Gambogin or *Gambogic Acid*, the resin of gamboge, according to Buchner has the formula $C_{30}H_{35}O_6$. It may be obtained by precipitating the filtered alcoholic solution of gamboge by water, treating the dried precipitate with ether, and evaporating the ethereal solution. It may be obtained less pure by treating the original gamboge with ether. Gamboge is a transparent, vitreous, brittle resin, breaking with a conchoidal fracture. The colour is hyacinth- or orange-red, and the powder bright yellow. It softens on heating and melts at 75°–80° C., solidifying to a glassy mass on cooling. It is tasteless, and, according to Hurst, has no purgative action. Gamboge-resin is readily soluble in alcohol, ether, and chloroform, but is only slightly soluble in petroleum spirit. Gambogin has well-marked acid properties, decomposing carbonates of the alkali-metals at a boiling heat. It dissolves in caustic alkalies with orange-red colour, and is precipitated in gelatinous flakes on acidulating the solution. On adding excess of common salt to the solution of gambogin in caustic soda, the sodium salt is thrown down as a red precipitate.

The *wax*, the portion of gamboge insoluble in ether but dissolved by alcohol, is described by Hurst as a soft brownish substance, melting readily and having slight bitter taste, and persistent bitter after-taste, with slight purgative action. It is soluble in caustic soda with brownish-yellow colour, being reprecipitated on adding an acid.

The *gum* of gamboge, according to G. H. Hurst, is a transparent, brownish mass, having a sweetish taste and slightly adhesive properties. It is soluble in water to form an opalescent solution, rendered clear by acids, and which is not precipitated by basic lead acetate, ferric chloride, mercuric chloride, borax, or alcohol. It appears to be a glucoside.

---

[1] The cylindrical variety of gamboge is produced by running the juice into bamboo-canes. On drying, the gamboge contracts, and consequently holes are often seen through the middle of the cylinders. Inferior gamboge often occurs in irregular masses weighing several pounds.

Gamboge dissolves in alcohol, in ether, and in ammonia. The ammoniacal solution produces a red precipitate with salts of barium, yellow with those of zinc, reddish-yellow with lead acetate, and brownish-yellow with silver nitrate.

The following analyses by Christison indicate the composition of commercial gamboge:—

	Pipe Gamboge from Siam.		Cake Gamboge from Siam.		Ceylon Gamboge.			
Resin, . . .	74·2	71·6	64·3	65·0	68·8	71·5	72·9	75·5
Gum, . . .	21·8	24·0	20·7	19·7	20·7	18·8	19·4	18·4
Amylaceous matter,	...	...	6·2	5·0	...	...	...	...
Woody fibre, .	...	...	4·4	6·2	6·8	5·7	4·3	0·6
Moisture, . .	4·8	4·8	4·0	4·6	4·6	...	...	4·8
	100·8	100·4	99·6	100·5	100·9	96·0	96·6	99·3

A sample of gamboge recently analysed by G. H. Hurst (*Pharm. Jour.*, [3], xix. 761) contained:—moisture, 2·50; mineral matter, 1·05; resin, soluble in ether, 66·05; wax, soluble in alcohol, 4·31; and gum, 26·03 per cent.; total, 99·94.

Commercial gamboge is liable to adulteration with *mineral matters* and *starch.* The *ash* should not much exceed 1 per cent. Starch may be detected by exhausting with alcohol, boiling the residue with water, and adding iodine to the cooled liquid, when the well-known blue coloration will be produced if starch be present. An emulsion, made by boiling the powdered sample with water, gives after cooling a green coloration with iodine in the presence of starch. It will be observed that the analyses of Christison of cake gamboge from Siam show a small proportion of starch.

Gamboge is not employed as a dye. It has a limited use in medicine as a purgative, and is employed as a yellow pigment in water-colour painting.

Dyes of Animal Origin.

The colouring matters contained in the blood, bile, and urine receive no practical application, and, so far as they require description, will be more conveniently considered in the sequel. Exclusive of colouring matters, such as *murexide* and *prussian blue,* which are prepared by complex chemical reactions from substances originally obtained from animals, the only dyes of animal origin which require description are *cochineal*, *lac-dye*, and *kermes*. These are derived from three distinct species of a peculiar tribe of insects called *Coccina*.

Cochineal is the female of the *Coccus cacti*, an insect which lives and propagates on certain kinds of cactus, especially the nopel, or *Cactus opuntia*, a plant which grows wild in Mexico, though the insects collected from the cultivated plant are the superior. The weight of the dried insect is about 0·1 grain, and hence 70,000 are required to produce 1 lb. of cochineal. The two chief varieties of cochineal are the white or *silver grain*, and the *black grain*. A third inferior variety, called the *granilla*, consists of very small insects, probably unimpregnated females. The silver grain, which is the finest kind of cochineal, probably consists of young females after impregnation, and the black grain of the mothers after the eggs have been laid. According to other descriptions, the colour of the grains depends on the method employed for killing and drying the insects (see *Jour. Soc. Chem. Ind.*, i. 181).

Carminic Acid, $C_{17}H_{18}O_{10}$, the colour-principle of cochineal, is prepared by Schützenberger by washing the cochineal grains (insects) with ether, to remove fat, and then treating them several times with warm water. On treating the filtered liquid with a slightly acid solution of lead acetate, the whole of the colouring matter is thrown down as a violet-blue precipitate. The concentrated filtrate deposits crystals of tyrosine, while the precipitate consists of carminate and phosphate of lead, with a little nitrogenous matter. This is removed by thorough washing with water, and the purified precipitate is suspended with warm water and treated with barely sufficient sulphuric acid to decompose the lead carminate, leaving the phosphate unattacked. The solution of the carminic acid thus obtained is evaporated to dryness at a temperature not exceeding 40°–50° C., and residue dissolved in absolute alcohol, which on evaporation and cooling yields the carminic acid in crystals. It may be further purified by dissolving it in water, filtering, evaporating, and recrystallising the residue from absolute alcohol or ether.

Carminic acid is a purple substance soluble in water, alcohol, carbon disulphide and benzene, and slightly soluble in ether. It does not melt or decompose at 135° C., and dissolves without decomposition in strong sulphuric and hydrochloric acids. Chlorine, bromine, and iodine readily destroy carminic acid, and nascent hydrogen reduces it to a leuco-body, which again becomes red on exposure to air.

The formula of carminic acid, according to Schützenberger, is $C_9H_8O_5$, but Hlasiwetz and Grabowski obtained potassium and barium salts corresponding to $C_{17}H_{18}O_{10}$, and found that when boiled with dilute acids carminic acid was split up into a sugar and carmine-red, a purple-red substance, which appears green by reflected light, and is cinnabar-red in powder. It is insoluble in ether, but soluble in water and alcohol with red colour.

Carminic acid dissolves in caustic alkalies with beautiful red colour. Sodium carminate crystallises in purple plates. An aqueous solution of carminic acid gives purple precipitates with baryta and lime water, barium chloride, lead acetate, and cupric acetate; with stannic chloride, a red precipitate; and with potassium oxalate or acid tartrate, an orange-red precipitate. Alumina removes the whole of the colouring matter from an aqueous solution of carminic acid, yielding a fine red lake, which when heated becomes crimson and purple. The addition of aluminium acetate or a little acid to the lake produces the same change of colour.

A decoction of cochineal behaves with reagents somewhat differently from a solution of pure carminic acid, owing to the presence of phosphates, tyrosine, &c. Acids produce a slight precipitate, and change the colour to a yellowish-red, while alkalies change it to violet. Lime-water, salts of copper, lead and zinc, and stannous chloride free from excess of acid give violet precipitates, while stannic chloride gives a scarlet coloration. Ferrous sulphate produces a violet-grey coloration and precipitate, and ferric acetate a brown precipitate, changing to olive-green. Alum changes the colour of a solution of cochineal to red, a precipitate being also formed; while aluminium chloride produces a reddish-violet precipitate, the supernatant liquor becoming crimson.

By heating carminic acid or carmine to 200° C. with water or dilute hydrochloric acid, or to 140° with strong sulphuric acid, an insoluble red body called ruficarmine or ruficoccin is formed.

Cochineal is somewhat liable to adulteration. A fraud said to be commonly practised at certain places consists in removing part of the colouring matter by a short immersion in water. After redrying, the partially exhausted material is sold as "black cochineal," or faced by agitation with talc, sulphate of barium, or sulphate of lead, and sold as "white cochineal." On powdering such a sample and treating it with water, the mineral adulterant will fall to the bottom of the liquid. Black iron sand, to the amount of 12½ per cent., has been recorded as an adulterant of black Teneriffe cochineal (*Jour. Soc. Chem. Ind.*, i. 144); and graphite and black oxide of manganese are other probable adulterants. According to Loewe, genuine cochineal leaves only 0·5 to 0·6 per cent. of ash on ignition.

In other cases the cochineal is subjected to an atmosphere of dry steam, and when the grains have swollen and become damp from the exudation of an adhesive juice they are rotated in a drum with the mineral adulterant, of which they take up from 10 to 12 per cent. On re-drying, the grains shrink up and assume their original appearance (Loewe, *Pharm. Jour.*, [3], xiii. 590).

The specific gravity of cochineal is a useful preliminary test of quality. Heavy samples are always inferior or adulterated. Partially exhausted cochineal is always deeply wrinkled, and does not, when treated with water, take up moisture equally, so that some of the insects or "grains" float, and others become only partly submerged.

To detect cochineal in alimentary substances, E. Lagorce recommends that the substance should be dissolved in water or weak alcohol rendered faintly acid with acetic acid. The liquid is then agitated with amylic alcohol, which is separated and evaporated in presence of water. The aqueous solution obtained is treated with a few drops of a 3 per cent. solution of uranium acetate, when a beautiful bluish-green coloration or precipitate will be produced if cochineal be present. Acids destroy this colour, with production of the orange tint of the carminic acid. In the case of wine, the amylic alcohol employed should be mixed with an equal measure of benzene, or, preferably, toluene, as otherwise œnolin will also be taken up, and will mask the reaction of the cochineal. Ammoniacal cochineal, which has been occasionally employed to colour wine, produces a rose-violet or violet-blue lake with uranium oxide. Logwood gives a somewhat similar reaction, but may be distinguished from cochineal by other means.

Cochineal has been occasionally adulterated with an extract of brazil-wood. This may be detected by treating the decoction with excess of lime-water, which completely precipitates the colouring matter of cochineal, while if brazil-wood be present the filtered liquid will have a purple or violet colour. Brazil-wood may also be detected by soaking cotton in the decoction and then immersing it in a warm solution of potassium bichromate, when the tissue will assume rather a deep colour if brazil-wood be present.

The assay of cochineal may be effected by boiling 1 gramme of the powdered sample for an hour with 1 litre of water and 20 drops of a saturated solution of alum. After cooling, the liquid is again made up to 1 litre, and the colour compared with that of a standard specimen similarly treated.

C. Liebermann (*Jour. Soc. Dyers, &c.*, i. 269) recommends that the cochineal should be exhausted as completely as possible with boiling water, and then precipitated with a slightly acid solution of lead acetate. The precipitate is washed with warm water, dried, and weighed, and the lead determined in an aliquot part of it. By deducting the amount of oxide of lead in the precipitate from the weight of the latter, that of the colouring matter is found. This method is open to the objection that phosphoric acid and other matters are estimated as carminic acid. Hence a more accurate result would be obtained by simply igniting the impure carminate of lead, and deducting the weight of the residue from that of the original precipitate. A still better determination of the colouring matter might probably be obtained by treating the moist lead precipitate with a slight excess of dilute sulphuric acid, filtering from the sulphate of lead, rendering the filtrate strongly alkaline with caustic soda, and running in a standard solution of potassium ferricyanide until the purple colour of the solution changed to a dull reddish-brown. The use of ferricyanide in alkaline solution for the assay of cochineal was suggested by Penny; but when the original decoction is operated on, as proposed by him, the results are not satisfactory.

Cochineal may also be assayed by a miniature dye-test. A suitable bath may be prepared from 1 gramme of finely powdered cochineal, 1 gramme of cream of tartar, 1½ gramme of alum, and 1 litre of water. 7 grammes of flannel should first be immersed and dyed to a full tone, and a second piece of the same weight then introduced, and allowed to remain till the bath is exhausted.

Cochineal is not used in cotton-dyeing. In dyeing silk it has also been almost entirely superseded by aniline-reds, and in wool-dyeing the azo-colours have to a great extent replaced it; though many dyers prefer to use cochineal or alizarin colours for all scarlets, since these dyes do not bleed and stain the neighbouring fibres like the azo-reds. Two distinct red shades are obtained with cochineal, according to the mordant used. *Cochineal crimson* is mordanted with cream of tartar and alum, with or without tin salts; while *cochineal scarlet* is mordanted with stannous chloride and cream of tartar or oxalic acid. Cochineal reds on wool are fairly fast to light, but become dull or bluish by the action of weak alkalies or soap, though the bright tone may be restored by immersing the fabric in water acidulated with acetic acid. A good purple colour can be obtained by dyeing wool mordanted with 2 per cent. of potassium bichromate in a slightly acid cochineal bath.

Fibres dyed with cochineal are turned orange-red by hydrochloric acid, the liquid becoming pink. Sulphuric acid turns both fibre and solution a bright pink. Caustic soda and ammonia give a purple solution. Alcohol has no action, and an acid solution of stannous chloride behaves much like hydrochloric acid alone.

Ammoniacal cochineal is prepared by leaving ground cochineal in contact with excess of ammonia, when a chemical action occurs which results, according to Schützenberger, in the formation of an amido-compound called carminamide. After several weeks the mixture is heated to drive off part of the ammonia, and is sent into commerce in the form of a thick paste. Instead of heating the product directly, it is sometimes mixed with about 40 per cent. of hydrated alumina, and the whole then heated till no odour of ammonia can be observed. When cold the mass is moulded into cakes.

Ammoniacal cochineal is distinguished from carminic acid by giving a beautiful purple precipitate (instead of scarlet) with "oxymuriate" of tin. The crimson, purple, and mauve colours it yields with mordants are not affected by acids so readily as those produced directly by cochineal. Ammoniacal cochineal is used in admixture with ordinary cochineal for producing the bluer shades of pinks.

Cochineal Carmine or *Carmine Lake* is a brilliant red pigment produced by precipitating a decoction of cochineal by alum or stannic chloride. Acid oxalate or tartrate of potassium may be used in conjunction with alum, but the employment of a compound of tin or aluminium appears to be essential to the production of the carmine. The employment of a decoction of cochineal itself, and not of carminic acid, is also a necessary condition, the nitrogenised matters being essential to its formation. The method by which cochineal-carmine is actually produced in practice is kept rigidly secret.[1] A sample examined by C. Lieberman (*Jour. Soc. Dyers, &c.*, i. 269) contained, after drying, 3·7 per cent. of nitrogen, only 0·25 per cent. of which could be expelled by boiling with dilute alkali. The remainder appeared to exist as proteïds, or probably in part as tyrosine.[2] The ash was white, and amounted to 8·1 per cent. 100 parts contained 43 of alumina and 45 of lime, 0·67 of oxide of tin, and small proportions of magnesia, alkalies, and phosphoric acid. The composition of the original carmine was probably approximately:—water, 17; mineral matter, 7; nitrogenous matters, 20; and colouring matter, 56 per cent.; with traces of wax.

---

[1] Several recipes, collected from standard works, have been published by M. Dechan (*Pharm. Jour.*, [3], xvi. 611). The English process is said to consist in boiling 1 lb. of cochineal and ¼ oz. of potassium carbonate with 7 gallons of water for 15 minutes. The heat having been withdrawn, 1 oz. of powdered alum is added, and the liquid stirred and allowed to settle. The clear liquid is decanted, ¼ oz. of isinglass added, and heat applied till a coagulum forms, when the liquid is stirred briskly and allowed to settle.

[2] As albumin and gelatin are sometimes employed in preparing carmine, it does not follow that the whole of the nitrogen present had its origin in the cochineal.

Cochineal-carmine is liable to adulteration with starch, kaolin, vermilion, red-lead, chrome-red, &c. These admixtures may be detected by treating the sample with dilute ammonia, in which a pure sample should be completely and readily soluble.[1] The solution of cochineal-carmine in ammonia yields no precipitate with ammonium oxalate, and the precipitate produced on adding an acid is a lake, from which the colouring matter can only be set free by heating with moderately strong mineral acid. If the ammoniacal solution of carmine be heated on the water-bath, with constant stirring, until entirely destitute of ammoniacal odour, the product is a deep ruby-red liquid which gives no precipitate with mercuric chloride, and becomes purplish on addition of ammonia. Vermilionette (page 168) can be recognised by treating the colouring matter with dilute sulphuric acid and agitating the liquid with ether, which on evaporation will leave the eosin in a condition ready for further examination.

The following analyses of commercial cochineal-carmine are by M. Dechan (*Pharm. Jour.*, [3], xvi. 511). The sample was treated with dilute ammonia, the liquid filtered, the ammoniacal solution evaporated, and the residue dried at 100°, and weighed. It was then ignited, and the ash weighed to obtain the combined aluminium, &c., the loss being regarded as colouring matter. The organic matter insoluble in ammonia appears to have consisted chiefly of starchy matters. In every case the ash was free from tin, and consisted of alumina and lime, with a trace of silica. No foreign colouring matter other than vermilion was detected.

		1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
Moisture,		22·1	16·1	2·0	22·3	20·2	23·5	8·5	10·0	21·2	13·0
Soluble in ether,	Colouring matter,	46·1	69·2	84·1	65·7	60·8	69·5	26·1	72·0	18·4	67·5
	Alumina, lime, &c.,	8·0	9·8	11·4	12·0	9·0	7·0	0·4	8·1	4·4	10·0
Insoluble in ether,	Organic matter,	21·8	2·5	18·5	0·0	9·8	0·0	0·0	8·0	52·4	9·5
	Ash,	2·0	2·4	34·0	trace	0·2	trace	14·6	1·9	3·6	trace
	Vermilion,	...	...	...	...	...	...	50·4	...	...	...

Carmine is employed by artists, paper-stainers, and fabric-printers.

---

[1] According to M. Dechan, tin spirits form with Biebrich scarlet a compound which very much resembles carmine physically and chemically, being, like it, soluble in dilute ammonia and insoluble in water. If Biebrich scarlet be present, white wool acquires a red-orange tint when boiled in the ammoniacal solution, whereas pure cochineal carmine communicates a reddish-purple shade. Biebrich carmine need not be looked for in the absence of tin.

Kermes is composed of the female of the *Coccus ilicis*, an insect found on the *Ilex* or *Quercus coccifera*, a shrub growing on arid, rocky soils in hot climates. The grains are about the size of a pea, globular, and almost smooth. Kermes of good quality has a deep red colour, agreeable odour, and rough, pungent taste. The red colouring matter is soluble in water and alcohol, and is either identical with or closely related to the carminic acid of cochineal (page 363). The decoction is turned yellow or brownish by acids, and violet or crimson by alkalies. Ferrous sulphate blackens it, probably owing to the presence of a small quantity of tannin from the oak on which the insect lives. Kermes dyes fabrics mordanted with alum a blood-red; with stannous chloride and cream of tartar it gives a cinnamon-yellow; and with salts of copper and cream of tartar, an olive-green. It requires about twelve times as much kermes as cochineal to produce the same scarlet with a tin mordant. Kermes is but little used in England.

Lac-Dye is the product of the *Coccus lacca*, which lives on the banyan and other trees, on the twigs of which the ova are deposited. From the mature and impregnated female insects a resinous substance exudes which encloses them. The twigs, with the attached resin and enclosed insects, are sold as *stick-lac*. If the resinous concretion be removed, powdered, and triturated with water, the greater part of the colouring matter dissolves, and the residue when dried is known as *seed-lac*. If this be melted and squeezed through cotton, it yields *shell-lac* or *shellac*. The following figures by Hatchett indicate the relative composition of these three lacs:—

	Stick-lac.	Seed-lac.	Shell-lac.
Resin, ...	68·0	88·5	90·9
Colouring matter, .	10·0	2·5	0·5
Wax, ...	6·0	4·5	4·0
Gluten, ...	5·5	2·0	2·8
Foreign bodies, . .	6·5	...	...
Loss, ...	4·0	2·5	1·8
	100·0	100·0	100·0

The exact method of preparing lac-dye is not generally known, but it is probably based on the treatment of stick-lac with a weak alkaline solution. The composition of the ash points to a precipitation with alum, or with lime to which some alumina has been added, probably to facilitate the washing and working up the precipitate (compare H. G. Glasspoole, *Pharm. Jour.*, [3], xii. 741).

The colouring matter of lac-dye has been investigated by R. E. Schmidt (*Jour. Soc. Dyers, &c.*, iii. 122), who terms it laccainic acid, and points out its close resemblance to carminic acid.

Laccainic Acid, $C_{16}H_{12}O_8$, forms a brownish-red crystalline powder or crust, appearing under the microscope in well-formed rhombic tables. It melts without decomposition at 180°. It is abundantly, though slowly, soluble in alcohol, and freely soluble in wood spirit, amylic alcohol, and glacial acetic acid. It is somewhat less soluble in water, with bluish-red colour, and is insoluble in benzene and petroleum spirit. It resembles carminic acid in being nearly insoluble in ether, but not precipitated on adding ether to its alcoholic solution. It is a well-defined dibasic acid, and in its reactions and the absorption-spectrum of its alkali-metal salts closely resembles carminic acid; but a difference exists between the absorption-spectra of the two substances when dissolved in strong sulphuric acid.

Schmidt gives the following results obtained by the analysis of two samples of lac-dye:—

	1.	2.
Moisture (expelled at 100°), . . .	9·0	11·26
Mineral matter, ...	15·7	18·24
Colouring matter, ...	10·4	13·20
Other organic matter, ...	64·9	57·30
	100·0	100·00

A good lac-dye should be soft enough to be broken with the fingers, and should powder readily under the pestle. The fracture should be deep in colour, not shining and resinous. When breathing on, it should emit a strong and peculiar odour. Samples which are hard and have a resinous fracture are usually poor in colouring matter, and contain an excessive proportion of resin. The amount of this constituent may be judged of from the bulk of the precipitate produced on diluting the alcoholic solution of the lac with water.

A superior variety of lac-dye is obtainable by treating stick-lac with weak ammonia, and adding stannous chloride to the solution, when the colouring matter is thrown down as a fine red precipitate. A *lac-lake* is obtained by substituting caustic soda and alum for the ammonia and tin salt in the above process. Lac-lake usually contains about 50 per cent. of colouring matter, 40 of resin, 9 of alumina, and 1 per cent. of impurities.

Lac-dye gives much the same colour as cochineal, but two or three times the quantity is requisite to produce the same effect. It is prepared for dyeing by mixing it into a paste with stannous chloride and hydrochloric acid, and hence the dye and mordant are used in the same bath. Lac-reds are considered faster to light and wear and to the action of weak alkalies than cochineal reds, though they are less brilliant than the latter. The two colouring matters are sometimes employed consecutively or in admixture.

RECOGNITION OF COLOURING MATTERS.

The number of dyes occurring in trade, and especially of those artificially prepared, is exceedingly great, and the difficulty of recognition consequent on their number and close resemblance is further increased by the practice of calling the same substance by several different names.

The methods of examining colouring matters with the view of identifying them require considerable modification when the dye already exists on a fibre or fabric, as the mordant and other conditions affect its character considerably. Hence the recognition of the dyes or fabrics will be described in a separate section (page 389). In the case of a concrete colouring matter it is desirable to ascertain the shade it communicates to wool or silk, as the colour which a dye will produce on a fibre can scarcely be guessed from its appearance in the solid state, and in many cases cannot even be predicted from the colour of the solution.

The great point of resemblance in the generality of coal-tar dyes is that they are "substantive colours," or, in other words, will dye silk and wool without a mordant. To ascertain whether the dye is of this character it is generally only necessary to heat a fragment of white wool or a skein of white silk in a solution of the dye; usually a neutral or faintly acid solution is the best, but with alkali-blue (page 230) and a few other dyes the stuff should be heated in the alkaline solution, and then removed and immersed in dilute acid, when the blue colour becomes fixed. Alizarin and purpurin are not substantive colours, and hence cannot be fixed on wool or silk without a mordant.

The identification of a coal-tar dye is much facilitated by a judicious employment of certain general reagents, which will suffice to define the substance as belonging to a certain class. The colour or absorption-spectrum of an aqueous or alcoholic solution of the dye is also a valuable indication, and water and alcohol may often be advantageously employed to effect a separation of mixed colours.

The following general methods of examination are of service in classifying the coal-tar colours:—

1. Agitate a small quantity of the dye with dilute sulphuric acid and ether. On separating the ether and evaporating it to dryness, a sensible residue will be left if the dye contained an acid dye, such as picric acid (or a picrate), a nitrocresolate (victoria yellow),

a nitronaphtholate (manchester yellow), aurin, an eosin, &c. The basic dyes are not removed from an acidulated aqueous solution by agitation with ether, and hence a complete separation of the above-named substances may be effected by a judicious employment of this method.

2. Another indication of the nature of a dye is obtained by adding weak caustic soda to the aqueous solution and warming the liquid. Basic coal-tar dyes, except those of the safranine class (safranine, safranisol), are precipitated, while the solutions of acid dyes usually remain clear.

3. E. Weingärtner recommends for the distinction of soluble acid from basic dyes a reagent prepared by dissolving tannin and sodium acetate in water. The preparation and application of this reagent are described on page 377.

4. By heating with acetic acid and zinc-dust, most basic coal-tar dyes are reduced with formation of colourless leuco-compounds, from which the colouring matters are reproducible only by the employment of moderately strong oxidising agents. The *azo-dyes* similarly yield colourless hydrazo-compounds, but these differ from the leuco-derivatives by regenerating the original colouring matters on mere exposure to air. Somewhat different results are obtained if an alkaline reducing agent is employed, and the method, which is of special value in studying azo-dyes, is described at length on page 211 *et seq.*

5. J. Spiller (*Chem. News*, xlii. 191) has shown that treatment of the sample with concentrated sulphuric acid affords a valuable means of recognising coal-tar dyes, which are none of them charred by its action, except under very severe conditions. To apply the test it is merely necessary to heat a few grains of the solid substance in a test-tube with concentrated sulphuric acid. Very frequently, useful information can be gained by observing the absorption-spectrum of the coloured liquid produced. The property of yielding a colourless solution with concentrated sulphuric acid, the liquid becoming coloured on dilution, is a characteristic reaction of several *quinoline dyes*, and does not occur in the case of dyes of most other classes. Tabular statements of the reactions of various dyes with concentrated sulphuric acid are given on pages 171, 185, 186, 193, 198, 205, 224, 232, 235, 239, 255, 273, 275, 277, 282.

6. In the case of basic dyes, the determination of the nature of the acid often materially assists identification. In most instances the basic dyes occur in commerce as hydrochlorides, but exceptions to this rule are by no means rare. To detect the salt-radical the solution of the dye should be precipitated with ammonia or soda,

and the filtered liquid acidulated with nitric acid and tested with silver nitrate. In some few cases, especially with safranine, the base of which is freely soluble in water, this method is not applicable, and it is necessary to add the silver nitrate to the acidulated solution of the original dye. Double chlorides of the dye-base and zinc may be recognised by the presence of zinc in the ash left on incinerating the sample. Common salt is very commonly present in dyes, and it is important not to mistake the chlorine existing in this form for that existing as the hydrochloride of a basic dye. Common salt will be left as a residue on igniting the dye. On ignition, the eosins leave residues the solutions of which contain more or less haloid salts of the alkali-metals, and hence precipitate silver nitrate. But these dyes are not basic, and the colouring matter (containing one or more halogens in organic combination) can be separated from the pre-existing common salt by agitating the acidulated solution of the dye with ether (compare page 385). The following is a list of those basic dyes liable to be met with in commerce in other forms besides that of hydrochloride :—

Name of Dye.	Formula of Base.	Form of Combination.
Magenta ; fuchsine ; rosaniline ; aniline red.	$C_{20}H_{20}N_3.OH$	Acetate.
Azaleine ; fuchsine.	$C_{20}H_{20}N_3.OH$	Nitrate.
Aniline blue ; triphenylrosaniline.	$C_{20}H_{17}(C_6H_5)_3N_3.OH$	Sulphate ; acetate (in alcoholic solution).
Methyl-violet.	$C_{19}H_{13}(CH_3)_5N_3.OH$	Zinco-chloride.
Benzyl-violet.	$C_{19}H_{12}(CH_3)_5(C_7H_7)N_3.OH$	Zinco-chloride.
Methyl-green.	$C_{19}H_{12}(CH_3)_6N_3.OH.CH_3Cl$	Zinco-chloride.
Iodine green ; night green.	$C_{20}H_{14}(CH_3)_6N_3.OH.CH_3Cl$	Zinco-chloride.
Spirit soluble green.	Do.	Picrate.
Benzaldehyde-green ; malachite-green.	$C_{19}H_{13}(CH_3)_4N_2.OH$	Oxalate ; zinco-chloride ; ferrico-chloride.
Phosphine.	$C_{19}H_{15}N_3$	Nitrate.
Mauve ; Perkin's purple.	$C_{27}H_{24}N_4$	Sulphate.
Nile blue.	$C_{18}H_{18}N_3O$	Sulphate.
Methylene-blue.	$C_{16}H_{18}N_3S.OH$	Zinco-chloride.

Nitrates, *acetates*, and *oxalates*, in a few cases in which they occur, can be sought for by the usual methods, in the filtrate from the precipitate produced on warming the dye with caustic soda. *Picrates* may be sought for in the same liquid, or the original solution may be strongly acidulated with dilute sulphuric acid, and agitated with benzene or ether. The mere detection of picric acid does not prove that the dye examined was a picrate, as free picric acid may have been added to the hydrochloride or double zinc salt of the base.

Many basic and other dyes are used in the form of *sulphonic acids*, and these latter bodies again are usually converted into metallic sulphonates. The sulphonates of potassium, sodium, and ammonium are the most common, but those of the metals of the alkaline earths are occasionally met with. Ammonium salts can be readily detected by the evolution of ammonia on warming the dye with caustic soda. Other sulphonates on ignition will leave metallic sulphates or sulphites, in which the metal can be readily identified. Of course, the presence of a sulphate in the ash does not prove the previous existence of a sulphonate, unless the absence of a sulphate in the original dye has been ascertained. This may usually be effected by adding barium chloride to the highly dilute aqueous solution of the dye. In the case of a coloured precipitate being formed, probably consisting of the barium salt of the sulphonic acid, this should be filtered off, washed, and digested with a solution of ammonium carbonate, which will convert a sulphonate of barium into barium carbonate, without affecting barium sulphate. On again filtering, and treating the residue with dilute hydrochloric acid, any white insoluble matter will consist of barium sulphate (compare page 385).

The *bases* of many acid dyes can be detected without igniting by precipitating a concentrated aqueous solution of the colouring matter with pure fuming hydrochloric acid, which almost always precipitates the free acid. After filtration, the base can be sought for in the filtrate.

For the detection of the *halogens* existing in organic combination in the eosins and some other dyes, the substance should be dissolved or suspended in water, and the liquid acidulated with dilute sulphuric acid and agitated with ether. The ethereal layer is then removed, evaporated, and the residue mixed with excess of quick-lime, free from chlorides, and then heated to redness in a combustion-tube. The product is treated with water, dilute nitric acid added in quantity sufficient to effect solution and leave the liquid slightly acid, the liquid filtered, and a portion of the filtrate tested with silver nitrate. If any notable precipitate is produced, chlorides, bromides, and iodides are then sought for in the usual way. In the aqueous liquid separated from the ethereal layer, metallic chlorides can be sought for directly by means of silver nitrate.

Nitro-compounds, used as colouring matters, are of a yellow or orange-red colour. When warmed with metallic tin (or stannous chloride) and hydrochloric acid, they are converted into colourless amido-compounds, which do not become again coloured on exposure to air. This behaviour distinguishes them, except acid naphthol-yellow, from the eosin dyes, but not from azo-colours. The latter, however, are usually sulphonates, and are not removed from their acidulated solutions by agitation with ether, as are the nitro-compounds, eosins, and most other phenolic dyes. The nitro-compounds also differ from the azo-dyes by dissolving in sulphuric acid to form yellow or colourless solutions, whereas with the latter far more brilliant and striking colours are obtained. The solutions of nitro-compounds, or fibres dyed with them, are but slightly altered by hydrochloric acid (distinction from yellow azo-dyes, which are reddened); while ammonia and caustic soda tend to darken or redden the colour (distinction from phosphine).

A considerable number of the colouring matters of commerce, possessing definite names, are by no means of a simple character, but are mixtures of two or more dyes. Mechanical mixtures may usually be recognised by spreading the powder on a piece of filter-paper and then floating the latter on some water or alcohol contained in a plate or flat capsule. Marks appear on the paper, and if the dye was of a simple character, are all of the same colour. On the other hand, if a mixture be under examination, the dye-particles dissolve with their respective colours, and the paper appears of two or more tints, according to the number of different colouring matters in the mixture. This appearance becomes very marked when the wet paper is held up to the light. It is even possible in this way to form an approximate notion of the relative proportions of the constituents of a mixture.[1]

When, as often happens with mixtures of azo-dyes, the constituents are too similar in shade to be recognised when dissolved side by side on filter-paper, the powdered dye should be sprinkled sparingly on the surface of pure, colourless, concentrated sulphuric acid contained in a porcelain dish. In many instances the particles will dissolve with marked differences in colour. Thus a mixture of orange II (mandarin) with croceïn scarlet, when sprinkled on sulphuric acid, will give carmine-red streaks alongside with others of indigo-blue colour. This method of examination is very sensitive.

CAPILLARY ANALYSIS OF COLOURING MATTERS.

Another useful method of examining certain dyes consists in dissolving the sample in the smallest possible quantity of alcohol, diluting the solution with rather more than its own measure of water, and then dropping the liquid on a piece of filter-paper, when concentric circles of different tones of colour will be produced if a mixture be under examination. Magenta may be conveniently examined in this way for violaniline, mauvaniline, or chrysaniline, and the same method may be employed for testing aniline blues and violets.

---

[1] This is sometimes of importance when it is desired to distinguish actual mixtures from dyes "ordered to shade," the latter being mostly of a simple character, but containing a slight addition of another dye, so as to give a required shade in dyeing. Thus most cheap violets contain a little magenta.

A more elegant and delicate application of capillary attraction has been made by F. Goppelsroeder (*Jour. Soc. Dyers, &c.*, iv. 5), who suspends a number of strips of Swedish filter-paper in such a manner that the lower ends of the strips dip into a series of small beakers containing solutions of the dyes to be tested. The water of the solution always rises to a greater height than the colouring matter. Picric acid stands next in capillarity, and if the method be applied to a mixed solution of picric acid and turmeric, after a time three zones may be distinguished. The highest narrow zone is produced by water only; below this there is a broad yellow zone containing picric acid; while in the lowest zone only the colouring matter of turmeric exists. On exposing the paper to fumes of ammonia or dipping it into weak alkali, the presence of turmeric will be indicated by the production of a brownish-red colour, while the picric acid zone will disappear. If the lowest zone be cut off, the colouring matter dissolved off with alcohol, and the process repeated with the solution obtained, the picric acid zone will be observed to be very narrow and faintly coloured. Interesting results are obtained when indigo-extract is examined in a similar manner. Traces of rosaniline may be detected in magenta by the same means. When an alcoholic solution of azuline (page 228) was examined by the capillary test, Goppelsroeder found three coloured zones to be produced, namely, pink, violet, and blue. In the alcoholic solution of the blue zone, silk was dyed a much purer blue than by the original colouring matter. It is evident that the method admits of various other applications.

Although mechanical mixtures are far the most frequent, more intimate mixtures are sometimes produced by co-precipitation, or evaporation of a mixed solution. In almost all such cases one of the constituents of the mixture possesses a greater affinity for a fabric than the other, and it is this circumstance which forms the principal disadvantage of such mixtures. If a small dye-bath be made up with the colouring matter, and small samples of wool or silk dyed successively therein until the bath is exhausted, the colouring matter, if simple, will give a shading down from one and the same colour. But in the case of a mixture each consecutive sample will have a different colour, and the first and last samples will be entirely different in shade. The division obtained in this way is often a very sharp one, and it becomes easy to recognise impurities in colour whether due to accident or intention. The test can be conveniently conducted in a wide test-tube or small beaker, combed wool being the fibre used to withdraw the dye from the bath.

TABULAR SCHEMES FOR RECOGNITION OF COLOURING MATTERS.

Several systematic methods have been described for recognising the various commercial colouring matters, especially those derived from coal-tar. These schemes have generally the defect of describing the colouring matters merely by their commercial names, and of being based merely on certain colour-reactions. Bearing in mind the great number of dyes now met with in commerce, and the rapidity with which these disappear and are replaced by new colours, and old ones under new names, no perfect scheme of examination can be expected. The best method in many respects is that of E. Weingärtner (*Jour. Soc. Dyers, &c.*, iii. 67), who arranges artificial colouring matters in three classes:—I. Basic colouring matters soluble in water; II. Acid colouring matters soluble in water; and III. Colouring matters insoluble in water.[1]

The soluble basic colouring matters are then distinguished from the acid dyes by a reagent prepared by dissolving 25 grammes of tannin and an equal weight of sodium acetate in 250 c.c. of water.

---

[1] The following table shows the solubility of certain coal-tar dyes in water and alcohol, as determined by A. Brunner (*Jour. Soc. Dyers, &c.*, iii. 194):—

Colouring Matters.	Reference Page.	Amount Dissolved by 100 parts of	
		Water.	Alcohol.
Aurin,	60	almost insoluble	40
Bismarck brown,	180	8	0·35
Corallin,	162	2	0·5
Dahlia blue,	...	4	1
Eosin,	167	2	1
Ethyl orange,	189	0·02	almost insoluble
Gentian violet,	...	1·5	8
Luteolin,	190	0·28	0·6
Magenta,	220	0·3	10
Malachite green,	241	4	5
Manchester yellow,	154	2	0·15
Methylene blue,	285	8	0·15
Methyl green,	240	7	0·25
Methyl violet,	234	2	1·5
Safranine,	256	0·6	0·4
Tropæolin OO,	189	0·05	0·1
Vesuvine,	180	2	0·2

This precipitates the basic dyes only. A few drops of the reagent are added to a 1 or 2 per cent. aqueous solution of the dye, and if any precipitation occur the liquid is heated, as certain sulphonated derivatives of triphenylmethane give precipitates at first which redissolve at a higher temperature.

The following are Weingärtner's tables for the recognition of artificial colouring matters. The group to which the dye belongs having been ascertained, the colouring matter may usually be identified by its special reactions. The figures in parenthesis after the names of the dyes show the pages on which more detailed information may be found respecting them.

TABLE I.—*Artificial Colouring Matters Soluble in Water. Basic Colouring Matters.*

The aqueous solution gives a precipitate with the tannin reagent.					
The primitive shade reappears.					The original shade does not reappear.
Red.	Yellow or Orange.	Green	Blue.	Violet.	
Magenta (220). Toluylene red (258). Safranines (254).	Phosphine (246). Flavaniline (245).	Malachite green (241). Brilliant green (239). Methyl green (240).	Methylene blue (285). New blue (260). Muscarine (260).	Methyl violet (234). Hofmann's violet (237). Mauveine (257). Amethyst (255). Crystal violet (236).	Chrysoïdine (179). Vesuvine (180). Auramine (240). Victoria blue (232). Methylene green (see below).
A	B	C	D	E	F

Observations.—After having reduced the basic colouring matter with zinc-powder and hydrochloric acid, the liquid should be filtered rapidly. It is very important to neutralise the filtered liquid with sodium acetate, since hydrochloric acid in excess may form with the basic colour acid salts, of different colour from the neutral salts.

The primitive shade does not appear on oxidation with the colouring matters in column F, but in certain cases oxidation produces different shades from the primitive. When Bismarck brown (vesuvine) and chrysoïdine are reduced, the di- and tri-amines are formed, which easily oxidise in the air with brownish-red colour. It is very important to distinguish this shade from the original, which is brown or yellow. After reduction and oxidation methylene-green gives a blue shade.

The oxidation of the reduced solution on the filter-paper may be facilitated by gently heating. Some colours oxidise with such rapidity that the original colour returns whilst filtering.

Methylene-green forms a dark green aqueous solution, which becomes quite colourless on reduction, but passes into sky-blue in presence of air. The solid substance dissolves in strong sulphuric acid with dark green colour.

TABLE II.—*Artificial Colouring Matters Soluble in Water. Acid Colouring Matters.*

The aqueous solution does not give a precipitate with the tannin reagent.					
The solution is decolorised.					The solution becomes brownish-red. The colour of the ammoniacal solution reappears on the paper.
The original colour reappears on paper.		The original colour does not appear.			
The aqueous solution is acidulated with hydrochloric acid, and treated with ether.		The colouring matter, when heated on platinum foil,			
The ether dissolves the colouring matter, and the solution immediately becomes colourless.	The ether remains colourless.	Deflagrates without formation of coloured vapours.	Burns quietly, or slightly deflagrates, giving off coloured vapours. Heat a piece of calico, not mordanted, in the aqueous solution.		
			The coloration of the stuff is fast to warm soaping.	The colour does not resist warm soaping.	
Phthaleïns (163). Eosins (167). Aurin (160).	Sulphonated rosanilines (226). Sulphonated indulines (249).	Nitro-colouring matters (137).	Azo-colours from benzidine, &c. (201).	Azo-colours (182, 191, 196). Tartrazin (288). Erythrosin (169).	Alizarin S (267). Alizarin blue S (269). Cœrulein S (74).
G	H	I	J	K	L

Observations.—*a.* The reduction of the acid yellow, orange, ponceau, and claret non-fluorescent colours requires special precautions. The best way is to treat with zinc-powder and hydrochloric acid, and afterwards to neutralise with sodium acetate, as has already been pointed out. The reduction will often be too slow if ammonia or acetic acid be used.

b. It is necessary, as before, to compare with great care the original colour with that which is produced by reoxidation, so that their identity or difference may not be mistaken. In the reduction of nitro- or azo-bodies diamines or amidophenols are formed, which by oxidation give dirty or brown shades. In the column K this remark equally applies to erythrosin, for when that colouring matter is reduced iodine is separated and fluorescin formed.

c. All the colouring matter not specified in *a* are reduced by zinc and ammonia.

d. When the acid colours are being reduced, the solution, as long as zinc-powder is present, should be colourless, or at most slightly yellow or red.

e. The nitro-derivatives of the azo-colouring matters and of fluorescein can be easily recognised by the formation of "Pharaoh's serpents" on heating a small quantity (0·5 grm.) on platinum foil.

f. In order to find the group NO_2 with certainty in a yellow colouring matter (*e.g.*, picric acid), it is necessary to add a little sodium carbonate.

g. It is very difficult completely to reduce alizarin S. It is therefore put in column L. The colour of the ammoniacal solution more often returns, but if the reduction has been carried too far that colour does not reappear.

TABLE III.—*Artificial Colouring Matters Insoluble in Water.*

The colouring matter is treated with water, and a little 5 per cent. solution of caustic soda added.						
The colouring matter dissolves.		The colouring matter does not dissolve. It is heated with 70 per cent. alcohol.				
The alkaline solution is filtered, treated hot with zinc-powder, and then poured on a filter-paper.						
The colour of the alkaline solution reappears.	The colour of the alkaline solution does not reappear, or the solution changes colour during the reduction, which colour lasts.	It is dissolved.				It is not dissolved.
		The alcoholic solution is not fluorescent. Add a little 33 per cent. soda solution.		The alcoholic solution is fluorescent. Add a little 33 per cent. soda solution.		
		The colour changes to red-brown.	The colour does not change.	The fluorescence disappears.	The fluorescence persists.	
Cœruleïn (276) (in paste). Galleïn (276). Gallocyanin (276). Galloflavin (276).	Canarin (288). Alizarin (276). Anthrapurpurin (272). Flavopurpurin (272). Nitroalizarin (267). Alizarin blue (268). Chrysamine (206). Solid green (158).	Indulines (248). Nigrosines (248). Rosaniline blue, 228. Diphenylamine blue (227).	Indophenol (259).	Magdala red (257).	Primrose, Cyanosin (171).	Indigo (294).
M	N	O	P	Q	R	S

In some respects the method of O. N. Witt (*Jour. Soc. Dyers, &c.*, ii. 64; *Analyst*, xi. 111) is preferable to that of Weingärtner.

When a doubt exists as to the identity of a colouring matter, it is often of service to dye some fibre with it, when its behaviour in an acid and alkaline bath, with and without mordants, and the colour and reactions of the material will render recognition certain and easy.

ABSORPTION-SPECTRA OF COLOURING MATTERS.

A valuable aid to the recognition of many colouring matters consists in the observation of the *absorption-spectrum*. For this purpose a pocket spectroscope will often suffice, but it is far better to employ a micro-spectroscope, furnished with a proper comparison-stage and reflecting prism, so as to allow of the spectrum of the colouring matter under examination being viewed in juxtaposition with the spectra of standard specimens of known origin.[1]

In comparing the standard liquid with the sample, it is necessary to regulate the light, so that neither spectrum shall suffer from excess of illumination. This may be done very effectually in the case of the object placed on the stage by the ordinary diaphragm attached to the microscope. The comparison-stage should be furnished with a slit giving a means of regulating the intensity of the light falling upon the comparison-prism. In using the microspectroscope, it is usual to employ the colouring matters in the state of solution, and it is not desirable to use too high a dispersive power, as in that case the absorption-bands are apt to be imperfectly defined. The nature of the solvent is by no means an unimportant factor in the results obtained, H. C. Sorby having found that the position of the absorption-bands was in certain cases sensibly affected by the nature of the solvent employed. When possible, it is always desirable to use aqueous solutions. The liquid to be examined with the microspectroscope is most conveniently placed in a small cell made by cementing a piece of barometer-tube (half an inch to an inch in length) to a glass microscope-slide by means of purified gutta-percha. The cement is not acted on by water, alcohol, or acid or alkaline solutions. The tube-cell being filled with the liquid, is covered with a thin piece of glass (microscope-cover). This is not absolutely necessary, unless some change is anticipated from the action of the air on the contents of the cell, but the precaution adds to the perfection of the definition. In recording the results of a micro-spectroscopical examination, Sorby has suggested the use of an *interference-spectrum*, which divides the visible spectrum into twelve equal parts. With such an arrangement the sodium line D comes very accurately at 3½, that is to say, in the middle of the fourth light-space; the bands being shaded off gradually on each side, so that the shaded portions are about equal to the intermediate bright spaces. On this scale, the positions of the principal lines of the solar spectrum[1] are about as follow :—

---

[1] A very serviceable form of micro-spectroscope is made by J. Browning, 63, Strand, W.C.

A	B	C	D	E	*b*	F	G
$\frac{3}{4}$	$1\frac{1}{2}$	$2\frac{3}{8}$	$3\frac{1}{2}$	$5\frac{11}{16}$	$6\frac{3}{16}$	$7\frac{1}{2}$	$10\frac{5}{8}$

In using the micro-spectroscope it is desirable to perform the operations and to subject the colouring matter to the action of reagents as much as possible in the very tube-cell used for the observation of the absorption-spectrum.[2]

In working with the micro-spectroscope it is very important to employ a strength of solution which will allow of the absorption-bands being well defined, and yet permit of as much light passing as is compatible with distinct absorption. The proper strength to use can only be ascertained by experiment in each case, the most convenient plan being to employ a concentrated solution first of all, and then to dilute it with the appropriate solvent, until the absorption-bands become weak, noting the spectrum after each change in concentration. Solutions should be kept in small test-tubes hermetically sealed, and filled as completely as possible with the liquids ; but even under such conditions many colouring-matters, especially those derived from plants, undergo profound change. Hence it is never safe to compare a recently prepared solution of a colouring matter with one which has been kept some time, unless it has been distinctly ascertained by previous experience that it is not liable to suffer change by long keeping. In employing the method as a means of differentiating colours it is highly important to compare the results with those produced by the pure colouring-matters.[3]

The absorption-spectrum of a liquid containing two distinct colouring-matters not having any chemical action on each other is identical with that which will be produced if the light traverse solutions of the two colouring matters in succession.[4] By employing a reagent which will destroy or modify one of the colours in a mixed solution without affecting the other, most valuable information may be obtained, and in researches on unknown colouring matters evidence is often thus afforded of the complex nature of the substance under observation.

---

[1] Mr Browning and Messrs Beck prepare this interference-spectrum.

[2] The solid reagents should be employed in the form of coarse powder or small grains, which can be added to the solution in the tube of the cell by means of a stout platinum wire, hammered out into a spatular form at one end. The reagent is best mixed with the liquid by means of a small platinum wire, of which the flattened-out part is bent up at right angles so as to form a miniature hoe. By the vertical motion of this in the cell very speedy solution and admixture of the reagent are obtained.

[3] A large number of observations, together with valuable hints in manipulation, and an attempt at a systematic qualitative discrimination of animal and vegetable colouring matters by the micro-spectroscope, have been published by H. C. Sorby (*Proceedings of the Royal Society*, No. 92, 1867).

[4] The well-known production of green by the mixture of blue and yellow is

P. Schoop (*Jour. Soc. Dyers, &c.*, ii. 71) has described means by which the absorption-spectrum of a colouring matter may be applied to its quantitative determination. Girard and Pabst (*Compt. Rend.*, ci. 156) have described and given drawings of several coal-tar dyes likely to be used for adulterating wines and syrups. In some cases they can be extracted and separated from the natural colouring matters by agitating the acidulated liquid with amylic alcohol.

In the case of dyed fibres the absorption-spectrum of the colouring matter may be conveniently examined by stretching a thread of the yarn or a very thin strip of the woven fabric across a blackened card or other black surface. The strip, which is used in place of a slit, is strongly illuminated, preferably by direct sunlight, and observed by a spectroscope with a widely-opened slit, and the telescope focussed on the card. In this manner very useful results are sometimes obtainable.

FLUORESCENCE OF COLOURING MATTERS.

Many colouring matters, *e.g.*, some of the eosins, magdala-red, purpurin, turmeric, resorcin-blue, &c., exhibit characteristic *fluorescence.* It is absolutely necessary that the liquid to be observed should be *perfectly clear*, as the presence of minute suspended particles often causes the production of a spurious fluorescence, which may lead to very erroneous conclusions. As a rule, the phenomenon of fluorescence may be observed by filling a small test-tube with the fluorescent liquid, holding it in a vertical position before a window, and observing the liquid from above against a dark background. Another plan is to make a thick streak of the liquid on a piece of polished jet or black marble, or on a glass plate smoked at the back, and to place the streaked surface in front

due to this cause. All yellow solutions transmit (and all yellow pigments reflect) the greater part of the red, yellow, and green light of the spectrum, while absorbing the blue and violet. Most blue liquids (and pigments) absorb the green rays very imperfectly, and it is only such impure blues which produce greens on admixture with yellows. If the light which has traversed such a blue solution, *e.g.*, indigo-extract (or which is reflected from such a blue pigment) be transmitted through a yellow liquid (*e.g.*, picric acid, or an ammoniacal solution of potassium chromate), the green portion of the spectrum will be almost the only part which survives the double absorption, and hence the light transmitted appears green.

of, and at right angles to, a well-lighted window. In this manner very faint fluorescence may be detected.

In some cases the following method of observing fluorescence may be advantageously employed. A cell is made by cementing a piece of barometer-tube, about ¾ inch in length and having an internal diameter of ⅛ inch, to a glass microscope-slide, by means of black sealing-wax. The open end of the cell must be well polished. On introducing a clear solution of any fluorescent substance, covering the cell with a piece of thin glass, placing the slide on the stage of a microscope, illuminating the tube-cell at the side by means of strong daylight, and looking down and observing the cell longitudinally by a low microscopic power, the liquid will appear more or less turbid, and of a colour dependent on the nature of the substance in solution. If no fluorescent body be present the field will appear perfectly black, as no light is reflected from the apparatus or the liquid. When desired, the *spectrum* of the fluorescent light can be observed by the micro-spectroscope. In some instances the spectrum thus obtained shows remarkable and characteristic bands.

On the fibre, the fluorescence of a dye is best shown by silk. Wool shows it sometimes, but on cotton the fluorescence can rarely be observed, owing to the rough character of the fibre.

EXAMINATION OF COMMERCIAL COLOURING MATTERS.

Dyes derived from coal-tar are usually definite chemical compounds, and hence when pure any particular dye should be of constant quality. The practice of mixing inert matters with coal-tar dyes, ostensibly to bring the colours to a definite standard of strength, but possibly with the additional object of direct adulteration, is unfortunately very common. In some cases, especially where the dyes are intended for exportation, the "standard" of strength is as low as 2½ per cent. of actual colouring matter, and in other cases, if not carried so far, adulteration is so generally practised that the pure colouring matters are almost unknown commercially (*Jour. Soc. Dyers, &c.*, iv. 70).

Among the adulterants most largely used are common salt, sulphate of sodium, and dextrin. Sulphate of magnesium is also employed, as also oxalic acid and certain oxalates, sugar, glucose, starch, &c. J. J. Hummel has described a sample of spurious magenta, consisting of crystals of acid oxalate of potassium, coated over with real magenta by steeping them in an alcoholic solution of the dye. Bronze-powder has been employed for adulterating certain aniline dyes.

Excess of water is very common in paste-dyes. The water itself may be determined by drying a known weight at 100° and observing the loss, but it must not be assumed that the residue represents the true colouring matter of the sample. The dry residue should be macerated with warm water in a mortar, and the solution filtered. The insoluble matter is then again weighed, or the dissolved matter is determined by evaporating an aliquot part of the solution, when a residue may be obtained, consisting of common salt, dextrin, glucose, glycerin, &c.

The presence of *mineral matters* generally may be detected and determined by burning a known weight of the sample and weighing the ash, but it must be remembered that metallic oxides and alkali-metal salts are left on the ignition of many pure dyes. This will be the case with sulphonated dyes, double zinc salts, the salts of acid colouring matters, and many others.

Common salt is so commonly employed for salting out coal-tar dyes from their solutions, that its presence in moderate amount in non-crystalline colouring matters must not be mistaken for an intentional addition with a view of increasing the weight. The direct application of silver nitrate to the solution must not be relied on for the detection of common salt unless the dye is such as will not contain the colouring matter in the form of a hydrochloride of the base, or yield an insoluble silver salt; but any chloride found in the ash left on igniting the sample probably existed as common salt, which can usually be recognised in the ash by its taste. The eosins leave chlorides, bromides, or iodides on ignition; but if the aqueous solution of the colouring matter be acidulated with dilute sulphuric acid and agitated with ether, the dye will pass into the ethereal layer, and after repeating the process till extraction is complete, the aqueous layer may be at once tested for chlorides by adding silver nitrate.

The presence of *sulphate of sodium* in the ash does not prove the existence of that salt as an adulterant of the original colouring matter, since sulphonated dyes usually leave a sulphate or sulphite of alkali-metal on ignition. The presence of a sulphate may be detected by the addition of barium chloride to the acidulated solution of the original sample, but the precipitate obtained often consists wholly or largely of the barium salt of the sulphonated dye. On filtering, and treating the precipitate with ammonium carbonate, the sulphonate will be dissolved with formation of barium carbonate, and on then washing the residue and treating it with dilute hydrochloric acid any barium sulphate will be left undissolved. Sodium sulphate is often present in the azo-dyes, and may be detected by saturating the aqueous solution with chemically pure chloride of sodium, when the sulphonated colouring matter will be precipitated, and the sulphate can be detected by adding barium chloride to the diluted and acidified filtrate.

The presence of magnesium in quantity in the solution or ash of a dye almost invariably indicates adulteration with *magnesium sulphate.*

Eosin dyes sometimes contain *carbonates of alkali-metals,* which will be detected by the evolution of carbon dioxide on acidifying.

Dextrin is usually recognisable by its odour on dissolving the dye in warm water, or on heating it in a test-tube. Where it is desired to ascertain the amount, from 1 to 2 grammes of the colouring matter should be washed with strong alcohol, the residue dissolved in the smallest possible quantity of water, and the solution filtered into a tared beaker containing a weighed glass rod. Alcohol is then gradually added as long as a precipitate is formed, whereby the dextrin is separated in flocks, which on stirring become attached to the sides of the beaker. The liquid is poured off, and the beaker and glass rod rinsed with rectified spirit, dried at 100° or slightly higher temperature, and weighed.

Sugar is not unfrequently employed as an adulterant of dyes. Crystallised magenta is often thus sophisticated.

On spreading out such a sample on a piece of white paper placed in a strong light, the large fragments may be recognised by their edges being less deeply tinted than the genuine crystals of the dye. When removed and cautiously washed with strong alcohol, the sugar fragments become nearly colourless, and may be identified by the odour of caramel produced on heating. The amount of sugar present may be ascertained in many cases with approximate accuracy by treating a known weight of the sample with absolute alcohol saturated with sugar, or with alcohol mixed with a little ether. A method of determining sugar in magenta and other basic dyes consists in precipitating the hot aqueous solution by picric acid. The filtered liquid is treated with basic acetate of lead, again filtered, the lead in the filtrate removed by sulphuretted hydrogen or sulphurous acid, and the sugar estimated polarimetrically, or inverted and determined by Fehling's solution.

Starch is left insoluble on treating the sample with cold water or alcohol, and may readily be recognised in the residue by its microscopical characters and the blue coloration produced with iodine.

Arsenic is sometimes met with as an impurity in magenta and other aniline dyes, though the frequency of its occurrence has been exaggerated. It may be detected and determined as described on page 225.

Antimony and other poisonous metals are sometimes employed for mordanting dyes, and irritation of the skin and other ill effects have been attributed to their presence. The subject has been discussed at length by J. R. Ashwell and H. Forth (*Jour. Soc. Chem. Ind.*, v. 226, 301).

Foreign colouring matters may often be recognised by a judicious treatment with solvents, or more systematically as described on page 375.

A valuable mode of ascertaining the actual percentage of colouring matter in a coal-tar dye consists in comparing its oxidising power with that of an equally concentrated solution of some pure dye of the same nature, used under precisely similar conditions. For this purpose two equal quantities of solution of sodium hyposulphite ($NaHSO_2$, page 306) should be introduced into small flasks containing a little petroleum burning-oil (kerosene). If magenta is the colour to be examined, a solution of rosaniline of known strength is then run in from a burette, while the flask is immersed in boiling water. The decolorisation is instantaneous, and the process is at an end when a permanent pink tint is obtained. An equal volume of the hyposulphite is then treated in an exactly similar manner with the solution of the sample to be tested, when the volume run in from a burette, compared with the measure of pure rosaniline solution previously employed, gives the requisite data for calculating the purity of the sample. When it is merely desired to compare the *relative* purity of two dyes, one of them is employed instead of the standard sample.

According to A. Stamm (*Jour. Chem. Soc.*, xxvi. 1263) 1 molecule of any aniline dye reduces the same volume of hyposulphite as 2 molecules of ammonio-cupric sulphate, and hence the method may be employed for ascertaining the molecular weights of aniline-derivatives. Hofmann's violet and Paris violet give absolutely identical results, and Paris green requires a volume of hyposulphite closely corresponding with the formula $C_{20}H_{17}(CH_3)_5N_3Cl_2+H_2O$.

Another useful quantitative method of examining many basic dyes consists in precipitating the solution by a standard solution of picric acid, in the manner described on page 145.

A simple and useful means of examining colouring matters is by making a solution and diluting it with water or alcohol (as the case may require) until the depth of colour is identical with that of a solution of known strength made from a standard specimen. The operation is conducted in a manner similar to the Nessler test for ammonia in water, or the colorimetric determination of carbon in steel.

One of the best methods of assaying aniline dyes, both for purity of tone and amount of colouring matter, is to compare the dyeing powers of the sample with those of a specimen of known purity. As a rule, from 1 to 3 grammes of each specimen should be dissolved in a litre of distilled water. Equal weights of unstoved white woollen yarn are suspended in each solution. The liquids are immersed in the same water-bath, which is heated gradually to 80° C. After an interval of one hour from the commencement, the temperature may be increased till the water boils, and after another half.hour the swatches of wool may be removed, rinsed with water, and their tints compared. When the wool is not dyed to an extent approaching saturation, it is easy to compare the relative depths of the tints. By employing 1 gramme of the standard, and several quantities, varying from 1 to 2 grammes, of the sample to be compared, it is easy to arrive at their relative dyeing powers. As a rule, water only is necessary, but some dyes are best tested in a slightly acid solution. In testing soluble blues, the wool should be heated to boiling in a dilute solution of the dye to which borax has been added, and the swatches then removed, rinsed with water, and the colour developed by immersion in dilute acid.

Another method of operating is to dissolve 0·5 gramme of the colouring matter in warm alcohol, and dilute the solution to 50 c.c., so as to obtain a 1 per cent. solution of the dye. Some water is heated nearly to boiling in a porcelain basin, and 1 gramme of fine white wool immersed in it till thoroughly wet. The wool is then removed, and 1 or 2 c.c. of the dye solution added, after which the wool is put back and the liquid heated for ten minutes. Should the whole of the colour be taken up, the wool is again removed, another addition of the dye solution made, the dyeing repeated, and so on till the wool is saturated. The volumes of dye-solutions decolorised by the wool in a series of experiments will be inversely as the purity of the samples of dye examined.

Some dyes, such as picric acid, cannot be completely withdrawn from their solutions, and in such cases the method is not applicable. In many instances, mixtures of dyes can be detected by dyeing successive small portions of wool in the same bath, when the colours fixed will often be notably different in tint, owing to the varying affinity of different dyes for the fibre (compare page 376).

Special methods of applying miniature dye-tests to certain colouring matters are described on pages 278, 312, 366, &c.

EXAMINATION OF DYED FIBRES.

W. Stein (*Dingl. polyt. Jour.*, ccx. 245) gives the following directions for testing the *fastness of dyes* on coloured fibres. They must be received with caution so far as the newer coal-tar dyes are concerned:—*Red* dyes should not colour lime-water or soap solution when boiled therewith, and the fabrics themselves should not be altered in colour by this treatment. A negative result when thus treated indicates the absence of brazil-wood, archil, safflower, sandal-wood, and many coal-tar dyes. *Violet* dyes may be considered unstable if they yield any considerable quantity of their colour when boiled with a mixture of equal parts of rectified spirit and water, and left to stand for fifteen minutes; or if, on boiling with dilute hydrochloric acid, they change in colour to brown or brownish-red, and colour the liquid red. Fast *blue* dyes should not give up any colouring matter when boiled with alcohol or warmed with a mixture of hydrochloric acid with water and alcohol. *Green* dyes when boiled with alcohol should not colour the liquid either blue, green, or yellow; and hot hydrochloric acid should not acquire a red or a blue colour from green fabrics. The fastest *yellow* is madder-yellow, which yields no colour to either water, alcohol, or lime-water used in succession. *Orange* dyes should not be dissolved from the fibre by boiling water or warm alcohol. *Brown* dyes may be considered unstable if they colour boiling water red, or give a yellow colour to alcohol when left in contact with it. If a *black* fibre, when boiled with dilute hydrochloric acid, colours the liquid merely yellow, it may be considered fast, as, for instance, tannin-black; and if the colour of a fresh portion is changed to brown when boiled with a solution of carbonate of sodium, there is probably only tannin-black present. If the fibre thus treated remains black or turns blue, it is probably bottomed with indigo under the tannin-black; while if the fabric colours hot dilute hydrochloric acid red, and is itself turned brown by the treatment, it is dyed with logwood-black, and may be considered unstable; but when boiled with acid the stuff becomes blue and colours the liquid red, it is logwood-black bottomed with indigo, and will have a certain degree of stability.

Recognition of Dyes on Fibres.

The recognition of artificial colouring matters on fibres is tolerably simple when only one dye is present, especially if no mordant has been employed. But when two or more dyes have been used, either in conjunction or succession, as is very frequently the case, the problem becomes more complicated, and the difficulty is further increased when the natural colouring matters and the mordants generally accompanying their use have to be taken into account.

In many cases, the identification of a dye is greatly facilitated by a knowledge of the mordant employed. Where the mordant is inorganic, its nature is best ascertained by examining the ash left on igniting the fibre. Organic mordants, such as tannin and albumin, are difficult to recognise in presence of colouring matters, and must be sought for by their special reactions. Fibres dyed with coal-tar colouring matters usually leave but little ash on ignition, as they require no mordant on silk or wool, and on cotton are usually fixed by means of tannin. On the other hand, alizarin and madder-dyes leave an ash containing a notable quantity of alumina or oxide of iron; while the ash of fibres dyed with cochineal, brazil-wood, &c., will be found to contain either alumina or oxide of tin. Logwood-black is mordanted with chromium and occasionally copper, while iron is a constituent of some blacks and violets, as also of prussian-blue. Lead is found in chrome-yellow, and is the base of vermilionette (page 168). Nickel is now employed for mordanting certain dyes, and antimony is also used.

The behaviour of the principal colouring matters on the fibre has been to a great extent described in the special paragraphs relating to the different dyes. Detailed and tabulated methods of examining dyed fabrics have been published by Fol (*Jour. Chem. Soc.*, xxviii. 193), Stein (*Zeitsch. Anal. Chem.*, ix., x.), Joffre (*Jour. Soc. Chem. Ind.*, i. 447, 496), and other writers. B. Martinon (*Jour. Soc. Dyers*, iii. 124) has published a scheme for the detection of dyes on *silk* (see page 394), and G. Dommerque (*Jour. Soc. Chem. Ind.*, viii. 216) a similar method for the recognition of dyes on wool. A more general tabulation of reactions has been published by J. J. Hummel (*Dyeing of Textile Fabrics*, Cassell and Co., Limited), and this has been supplemented by R. Lepetit (*Jour. Soc. Dyers, &c.*, iv. 133), the translator of Hummel's work into Italian (see page 398).

EXAMINATION OF RED-DYED FIBRES. The *red dyes* are very numerous and often difficult to identify, and hence the following hints may be found useful. They will in many cases also be found in the tables commencing on pages 395 and 399, but are given here for convenience of classification and reference.

1. Boiling *alcohol* removes magenta, safranine, corallin, aurin, spirit eosins, archil, santal- and bar-wood, but does not greatly affect tissues dyed with red and claret azo-dyes, acid magenta, magdala-red, alizarin and madder-dyes, cochineal, safflower, brazil-wood, lac-dye, or kermes, and does not extract soluble eosins if well dyed. Purpurin is partially extracted, colouring the alcohol red.

Magenta, safranine, and archil also colour the alcohol red, and santal-wood yellowish-red, but the others form yellowish, brownish, or nearly colourless solutions. On evaporating the alcoholic solution to dryness, and treating the residue with strong sulphuric acid, magenta yields a yellow or brown solution, but safranine produces a fine green colour, changing through various tints by gradual addition of water.

2. Magenta may be distinguished from archil-red and aurin by treating the fibre with *amylic alcohol.* This is coloured bluish-red by magenta, pink or violet by archil, and yellow by aurin. On shaking the coloured amylic alcohol with ammonia, it is decolorised if the dye be magenta, but the colour will be unchanged if archil, and turned bluish-red if aurin be the colouring matter present.

3. *Ether* removes corallin, aurin, and eosin more or less perfectly. Tissues dyed with turkey-red acquire a dull cherry-red colour, and the ether leaves a brilliant scarlet fat on evaporation. This, when boiled with caustic soda, yields a purplish-blue solution, from which acids precipitate orange-coloured flakes of alizarin.

4. By boiling with *ammonia,* corallin, aurin, and the eosins are usually dissolved from the tissue, the liquid being coloured pink or red.[1] On removing the tissue, and agitating the liquid with ether and an acid, the colouring matters are extracted from the aqueous liquid, and may be detected in the ethereal solution by separating it, and evaporating to dryness or agitating with ammonia. Safflower colours ammonia salmon-tint. On the azo-reds ammonia usually has no action, and the same remark applies to alizarin and magdala red. Fibres dyed by magenta and acid magenta are decolorised, and safranine gives a pink solution. The vegetable colouring matters usually behave as with soda.

5. On moistening the fibre with a dilute solution of *caustic soda* (5 to 10 per cent.), the colour due to rosaniline is very gradually destroyed. Safranine remains unchanged, but safflower is turned pale yellow, the original tint being restored by an acid. Cochineal gives a purple solution. Aurin, corallin, and eosin behave as with ammonia. From fibres dyed with brazil-wood caustic soda extracts much of the dye, cotton being almost decolorised, and the solution becoming bluish-red. Barwood and santal-wood gives no colour to

---

[1] When boiled with concentrated solution of caustic potash (20–40 per cent.), Eosin G gives an orange-red solution, which on continued boiling becomes purple, and finally blue, with a strong green fluorescence. Neither the colour nor the fluorescence is changed by dilution. Eosin B, when similarly treated, gives a bluish-violet solution, with pale green fluorescence. On dilution, the liquid becomes reddish-purple. Eosin BN, when boiled with potash gives eventually an olive-green non-fluorescent solution.

the liquid, but the fibre becomes purplish. With archil the fibre becomes bluish-purple, and with magdala-red a dirty violet.

6. On treating the tissue with moderately strong *hydrochloric acid* (sp. gr. 1·11), magenta is turned brown or yellow, but the colour is restored by washing with water. Hydrochloric acid does not change the colour of fibres dyed with acid magenta, but the liquid acquires a faint bluish-red colour. Safranine is unchanged by dilute acid, but with strong acid a blue colour is produced, restored to red by washing with water. Turkey-red is unchanged. The azo-reds are usually (but not invariably) turned more or less violet, a coloured liquid being extracted. Of the azo-dyes from benzidine, &c., fibres dyed with congo-red are turned blue-black by hydrochloric acid, and delta-purpurin, benzo-purpurin 11 B, and congo-corinth give similar reactions. With rhodamine the fibre is turned a dirty brick-red, without the liquid being coloured. The original hue is restored by washing. The eosins are turned yellow or brownish-yellow. Tissue dyed with brazil-wood is turned bright orange by dilute acid, and corallin, aurin, and cochineal yellow. Ammoniacal cochineal, however, is unchanged by dilute acid.

7. On boiling the tissue in an aqueous solution of aluminium sulphate the liquid will become reddish with most dyes, and in the case of madder-red or purpurin will show a green fluorescence. On adding an equal measure of acid sodium sulphite to the red liquid, the solution will be bleached if the dye be magenta, safranine, corallin, safflower, brazil-wood, or santal-wood, but not bleached if the colour be due to archil, cochineal, lac-dye, or kermes.

8. On igniting the tissue, the red coal-tar dyes usually leave very little ash, as they require no mordant on silk and wool, and on cotton are usually fixed by means of tannin. On the other hand, madder-red and pink leave an ash containing a notable quantity of alumina, and the ash of tissues dyed with cochineal or brazil-wood, or other dye-woods, will usually be found to contain either alumina or oxide of tin. Murexide, which is not now employed, used to be fixed by compounds of lead or mercury. Of course, the latter metal did not appear in the ash. Vermilionette is a lead compound of eosin, but its use is chiefly restricted to pigments.

RECOGNITION OF THE CONSTITUENT DYES OF COMPOUND SHADES. —The following hints, chiefly by G. Dommerque (*Jour. Soc. Chem. Ind.*, viii. 216), will be found of service for identifying the constituents of mixed dyes on wool.

Garnet Shades contain red as the predominating constituent. Bright garnets are a mixture of yellow and red. In examining them, moisten the fibre with hydrochloric acid. If turned yellow, the yellow constituent was manchester yellow (dinitro-cresol), this being the only yellow which is dyed in a neutral bath, and which does not precipitate the salts of rosaniline. If on application of hydrochloric acid the shade becomes slightly bluer, the colour is probably produced from acid-magenta and naphthol-yellow or chrysoïn; while if it turn violet acid-magenta and orange IV (or an allied orange or yellow azo-dye) are indicated. All bright garnet shades lose their red colour when moistened with ammonia, yellow remaining. The rarely occurring shades produced with bordeaux and amaranth are not altered by ammonia, but become violet-blue or blue when touched with sulphuric acid.

Maroons and Compound-Red Shades are examined by moistening the fibre with ammonia. If it become green, the fibre was probably dyed with a mixture of acid-magenta and sulphonated indigo. If turned yellow, the same portion of fibre should be slightly washed and treated with hydrochloric acid, when if the yellow become violet, orange IV or other azo-orange or yellow is indicated; while if rendered slightly blue, chrysoïn or naphthol-yellow is the probable yellow constituent. If the yellow colour produced by ammonia remain unchanged on subsequent treatment with hydrochloric acid, the presence of acid-green, acid-violet, and acid-magenta is probable. If orange IV be also present, the fibre becomes reddish-violet with hydrochloric acid. If the colour be unaffected, or simply rendered paler by treatment with ammonia, the dye may be either :—a mixture of an azo-red, indigo and orange IV, in which case it becomes slightly violet with hydrochloric acid (if this acid produces no change, chrysoïn is probably present); or logwood, becoming red with hydrochloric acid. If dyed with a mixture of logwood and orange IV, acid changes the colour to violet-red or garnet.

Scarlets.—Cochineal-scarlets are turned violet by caustic alkalies, and the ash contains tin; alkalies turn artificial scarlets yellow.

Dark Blues and Purples.—Complete decolorisation on moistening the fibre with ammonia points to a probable mixture of acid-green, acid-violet, and acid-magenta. If the red be removed from the fibre and the blue left, the latter is probably indigo and the former acid-magenta. If the shade become slightly pale the dye is probably a mixture of indigo and an azo-red, in which case the shade will not be appreciably changed on further testing the fibre with hydrochloric and sulphuric acid. Logwood will colour the acid red, and the ash will contain chromium. In shades produced by mixtures of logwood, sulphonated indigo, and acid-magenta or an azo-red, the constituents are difficult to identify.

Dark Greens.—If only the yellow remain on moistening the tissue with ammonia, a mixture of acid-green and acid-violet with naphthol-yellow or picric acid may be suspected. Should the shade if changed become paler, the fibre is moistened with hydrochloric acid, when logwood will colour the acid red. If the fibre become red or violet-red, and the ash contains chromium, the yellow constituent is probably fustic. If, on treatment with the acid, the yellow disappears and the blue remains, a mixture of indigo with picric acid or naphthol-yellow is probably present.

Olives, when moistened with ammonia, turn yellow if dyed with a mixture containing acid-green and acid-violet, and on treating the fibre with hydrochloric acid it will become garnet if the yellow constituent be orange IV, and yellow-brown if it be chrysoïn. Olives containing indigo become slightly bluer with ammonia.

Mode Colours are liable to contain a great variety of dyes, perhaps the most common being archil, archil-substitutes (azo-reds), azo-oranges, and acid-magenta.

TABLES OF REACTIONS OF DYED FIBRES.

The following tables, by B. Martinon (*Jour. Soc. Dyers*, iii. 124), for the recognition of dyes on silk, are not so complete as some other schemes, but are more systematic, and involve the use of certain reagents, such as solution of bleaching powder and nitrous acid, which are sometimes neglected. The reagents employed are:—

Caustic Soda Solution.—1 part in 10 of water.

Hydrochloric Acid.—Acid of 1·16 sp. gr. diluted with an equal volume of water.

Calcium Hypochlorite.—40 grms. of bleaching powder dissolved in 1 litre of water and the liquid filtered.

Nitrous Acid.—20 grms. of sodium nitrite and 15 grms. of sulphuric acid (sp. gr. 1·845) are respectively dissolved in 1 litre of water. Equal volumes of these solutions are mixed when required.

Potassium Cyanide.—50 grms. in 1 litre of water.

Nitric Acid.—Acid of 1·32 sp. gr., diluted with an equal volume of water.

Sodium Carbonate.—1 part of the salt in 10 parts of water.

From 10 to 15 c.c. of the required reagent should be placed in a porcelain dish, the silk to be tested immersed in it, and the change of colour observed. After two to three minutes, the silk is taken out and well washed. Another portion of the silk should be simultaneously placed in clear water, in order that any change in colour by the action of the reagent may be better observed. To ensure absolute certainty, it is also advisable to dye a piece of clean silk with the detected dye, and to repeat the experiments on this from the beginning.

YELLOW DYES.

HCl	No action.	NaOH	No action. HNO$_3$	Green-yellow, then dirty green. On washing, slowly faint yellow			Saffron (348).
				Faint brown; on washing again yellow			Quinoline Yellow (174).
			Alters shade slightly	Alkaline liquid brownish-yellow, with faint green fluorescence	HNO$_3$ and washing	No action	Fustic and SnO$_2$ (345).
						Brownish-yellow	Fustic and Al$_2$O$_3$ (345).
				The alkaline liquid is yellow. With HNO$_3$ silk becomes yellowish-brown			Quercitron and SnO$_2$ (343).
			Brown-yellow	CaOCl$_2$	Brown; with HNO$_3$ brownish-yellow		Sumach and Al$_2$O$_3$ (107).
					Brown; with HNO$_3$ chestnut-brown		Alkanet (337).
			Reddens somewhat. CaOCl$_2$ without action				Heliochrysin (138).
			Turns red and then decided brown; on washing again yellow. With HNO$_3$ more yellow				Nitro-alizarin (267).
			Faint greenish-yellow. CaOCl$_2$ decolorises. On washing remains a faint yellow colour				Phosphine (245).
			Pure yellow. CaOCl$_2$ bleaches silk slowly				Chrysoïdine (179).
		H$_2$O	Bleached on washing. CaOCl$_2$ without action				Quercitron and Al$_2$O$_3$ (343).
			Bleached by washing, and remains brown-yellow. With CaOCl$_2$ silk becomes brown-yellow				Weld and Al$_2$O$_3$ (347).
	Decolorises or bleaches considerably	NaOH	Decolorises	Colour does not return after washing			Chrome Yellow.
				Colour reappears on washing	Na$_2$CO$_3$ without action		Auramine (244).
					Na$_2$CO$_3$ decolorises		Flavin (342).
			Reddens				Aurantia (156).
			Changes slowly into orange-yellow. With KCy	Reddish-brown			Picric Acid (146).
				No action			Naphthol Yellow S (156).
			Scarlet				Chrysamine (206).
	Intense red.	HCl coloured violet-red. With water silk turns brownish-red, then again yellow					Orange IV (184).
	Reddish-brown	NaOH	The silk becomes reddish-brown. HNO$_3$ without action				Turmeric (360).
			The NaOH is coloured orange. HNO$_2$ chestnut-brown				Young Fustic (347).
	Dark yellowish-brown colour; on washing it remains a brownish-yellow. With NaOH chestnut-brown, with CaOCl$_2$ orange						Alkanet and Al$_2$O$_3$ (337).
	Reddish; with NaOH chestnut-brown. CaOCl$_2$ and HNO$_2$ without action						Citronin (190).
	Orange. NaOH faint brown. With CaOCl$_2$ colour becomes slightly red						Amidoazobenzene (179).
	Orange; with NaOH scarlet. CaOCl$_2$ wood colour. With HNO$_2$ reddish-brown						Chrysoin (184).

ORANGE YELLOW DYES.

HCl	Without action	NaOH	No action	Turmeric (360).
			Reddens and turns decided brown. HNO_2 without action	Nitroalizarin (267).
	Scarlet, more or less brownish	NaOH	Scarlet	Orange I and II (184).
			Pure yellow	Orange III (188).

RED DYES.

HCl	No action	NaOH	Turns somewhat brown			Roccellin (192).
			Violet-red	HNO_2 No action	HNO_3 Brownish-red	Magdala Red (257).
				No action	Reddish-violet	Archil substitute (192).
			The silk becomes violet	Bleached and turned yellow		Archil (320).
	Bluish-violet	NaOH	Scarlet. $CaOCl_2$ no action			Congo Red (206).
			Pale violet-red. $CaOCl_2$ decolorises			Safranine (256).
	Reddish-violet. NaOH decolorises					Acid Magenta (226).
	*	NaOH	Decolorises slowly; silk remains faint rose-colour, and becomes red on washing			Magenta (224).
			No action			Benzopurpurin (207).
			Silk becomes lilac			Ammoniacal Cochineal (367).
	Bright yellow	NaOH	Violet-red	$CaOCl_2$	Na_2CO_3 No action. Solution in boiling alcohol is fluorescent	Eosin (168).
					The Na_2CO_3 becomes pale violet	Erythrosin (169).
					First violet, then slowly loses colour	Cochineal (366).
					No action. The Na_2CO_3 becomes violet	Alizarin (264).
				Silk decolorised; the soda solution is coloured brownish-red		Safrosin (169).
	Silk more or less brownish-yellow	NaOH	No action	HNO_2 No action.		Silk Scarlet (192).
				Wood colour		Peonin (162).
			Silk black-brown			Scarlet (192).
			Silk scarlet. HNO_2 slowly colours it yellow			Red Woods (333).
	Silk decolorised	NaOH	Silk reddish-violet	HNO_3 Decolorises		Primrose (167).
				Silk becomes cream-coloured		Bengal Red (169).
			Silk grey			Murexide (144).

* Some coloration or direction appears to have been omitted at this point.

BLUE DYES.

HCl	No action.	NaOH	Silk dirty green, the soda is coloured yellow					Indigo Carmine (313).
			Silk at first dirty green, then loses colour. The alkaline solution gives a blue precipitate with HCl and ferric chloride					Prussian Blue (409).
			Silk red, more or less of violet shade On washing, it again turns blue	$CaOCl_2$	Silk decolorised	HNO_3	Silk bluish-grey	Spirit Blue (228).
							Silk faint lilac	Alkali Blue (230).
							Silk black-blue and then chestnut brown	Water Blue (231).
							No action	Azo-Blue (208).
			Shade changes to red, but by washing again becomes blue					Induline (250).
			No action	$CaOCl_2$	Silk slowly becomes grey. With HNO_3 reddish-grey			Basle Blue (252).
					No action. With HNO_2 silk becomes green, with HNO_3 a dirty green			Methylene Blue (287).
					Slowly decolorises. With HNO_3 silk green, then cream-coloured			Indigo (312).
	Pale chestnut-brown. With H_2O green, then greenish-blue							Indophenol (259).
	Reddish-brown. With H_2O blue							Alizarin Blue (269).
	Scarlet. With water it turns first violet, then blue							Resorcin Blue (159).
	Green. With water blue colour reappears instantly							Victoria Blue (233).

VIOLET DYES.

HCl	Blue, then bluish-grey and orange. Water again produces violet. NaOH reddens	Methyl Violet (236).
	Blue. With water original colour reappears. With NaOH blue	Mauvein (257).
	Reddish-brown	Gallein (73).

GREEN DYES.

HCl	No action. Fibre contains Fe_2O_3		Resorcin Green (158).
	Silk grey, HCl coloured red-brown. On washing grey colour remains		Cœrulein (74).
	Silk yellow. NaOH	Decolorises. Silk remains unchanged on heating to 100°	Malachite Green (241).
		Decolorises. On heating to 100° silk is coloured violet	Methyl Green (240).
	Silk green-yellow. With NaOH brown-grey. On washing original colour does not reappear		Aldehyde Green (287).

The tables of Hummel and Lepetit, already referred to (page 390), together constitute the most complete description of the reactions of dyes on fibres yet compiled, and as the present section would be imperfect if these were omitted, they are given with a few modifications in the following pages. The dyes (about 60 in number) given by Lepetit but omitted by Hummel are distinguished by the letter *L* prefixed to the name, while those in Hummel's tables are distinguished by the letter *H*. The figures in parentheses following the names of the dyes refer to the pages of this volume on which further information may be found. In the case of dyes which are fully described elsewhere, many of the special reactions and remarks are omitted.

The following abbreviations are employed for the names of firms identified with the production of certain dyes:—

B. A. S. F. Badische Anilin und Sodafabrik.
M. L. & B. Meister, Lucius, & Bruning (Höchst).
Act. Ges. Berlin. Actiengesellschaft für Anilinfabrikation in Berlin.
D. & H. Durand & Huguenin (Basle).
B. S. & S. Brook, Simpson, & Spiller (London).

Various other abbreviations are employed with the object of saving space, but they will probably be readily intelligible without special description.

G. Dommerque has recently published (*Jour. Soc. Chem. Ind.*, viii. 216) a systematic method of recognising dyes on wool. In cases where his observations are not in accordance with those of Hummel or Lepetit, both statements are given in the tables, those of Dommerque being in parentheses. In all cases the reactions are quoted on the authority stated, though occasionally they are not in accordance with the statements made in other parts of this work.

The reagents applied are concentrated hydrochloric acid (sp. gr. 1·11), concentrated sulphuric acid, caustic soda (10 per cent. solution), strong ammonia, a hydrochloric acid solution of stannous chloride, alcohol, and certain special reagents. The experiments are best made by treating portions of the fibre or fabric in small porcelain dishes, which can afterwards be inclined so as to allow the liquid to drain to the side and permit the ready observation of any colour it may have acquired. In some cases, as when fluorescence is to be looked for, it is desirable to employ test-tubes instead of porcelain capsules. Where nitric acid is employed, it should be applied to the fabric with a glass rod, when any change in the colour of the spot touched will be readily seen.

[TABLES.

I. RED COLOURS.

Colouring Matter.	HCl	H_2SO_4	NaOH	NH_4OH	$SnCl_2$ and HCl	Alcohol.	Special Reactions and Remarks.
H. Magenta (220).	F. and soln. yel.; colr. restored on washing.	As with HCl	F. at first paler, afterwards nearly colourless, especially on heating.	F. decolorised.	Almost entirely decolorised on boiling; col. partly restored on washing.	A bluish-red liquid readily extracted.	See also page 391.
H. Acid magenta. B. A. S. F. (226).	Faint bluish-red liqd. extracted; col. of fibre unchanged.	As with HCl	F. decolorised in the cold.	F. decolorised, col. gradually restored on exposure to air.	Colr. largely extracted on boiling.	Very little col. extracted.	
H. Safranine. B. S. & S. (226).	Dil., no action; conc. f. becomes blue.	F. at first blk., which soon changes to green.	Soln. pink.	As with NaOH	Decolorised on heating, liqd. colourless.	Col. extracted, red fluorst. soln.	
H. Magdala red (257).	No change.	No change.	No change.	No change.	Little action, f. slightly blue.	Very slightly extracted. Sol. fluorst. pink.	To detect magdala red on silk dyed with a mixture of magdala red and eosin, extract with boiling alcohol, which dissolves out the eosin, and test the solution in the ordinary way. Wash the silk and test for magdala red with acids and alkalis.
H. Eosin A. B. A. S. F. (167).	F. pale yellow.	F. at once bright yellow.	F. yellow, liq. pink fluorsct.	F. yel., liq. yel. fluorsct.	F. orange-yel., sol. pale yel.	*Soluble* eosins not extracted if well dyed. *Spirit* eosins readily extracted by absolute alcohol.	See also page 391.
H. Methyl-eosin (171).	F. yellow.	F. yellow.	F. pink, liqd. pink fluorsct.	As with NaOH	...	Pink fluorsct. soln.	
H. Phloxin J. (171).	F. yellow.	F. yellow.	F. and liqd. pink.	F. and liqd. pink.	F. yellowish on boiling.		

I. RED COLOURS—*continued.*

Colouring Matter.	HCl	H_2SO_4	NaOH	NH_4OH	$SnCl_2$ and HCl	Alcohol.	Special Reactions and Remarks.
H. Erythrosin (171).	F. brn.-yellow.	F. yellow.	F. and liqd. pink (or little changed).	F. orange on boiling.			
L. Rhodamine. B. A. S. F. (173).	F. dirty brick-red, liqd. colourless. On washing original colour restored.	As with HCl	F. somewhat darker and bluer, liquid colourless.	Fibre as with NaOH, liquid slightly pink and fluorsct.	In the cold no action. On heating fibre dirty brownish-red, liq. slightly pink.	Slightly extracted, forming fluorsct. solution.	HNO_2; No action. HNO_3: Orange-red spot, disappearing on washing. Stands boiling with soap very well.
H. Aurin (161).	F. yellow.	As with HCl	Sol. bright red.	As with NaOH	In the cold soln. yellow.	Colour extracted.	
H. Croceïn scarlet 7 B. F. Bayer & Co. (196).	Fibre at first violet, liquid colourless. On standing, f. becomes blue, liq. grn-blue.	Concent. acid, fibre and sol. blue.	Col. of f. blue.	...	F. decolorised.	Little or no action.	HNO_3 gives at first a blue spot, which changes to bright yellow with a greenish-blue border.
H. Biebrich scarlet. Kalle & Co. (197).	F. violet, liqd. colourless. On standing, liq. becomes grn.-blue.	Fibre and soln. green.	F. dark bluish-red, liquid colourless.	No action.	F. decolorised.	Little or no action.	HNO_3 gives at first a blue spot, which changes to brown with a blue border.
H. Patent Fast red. B. A. S. F.	F. darkened, liq. slightly tinged red.	F. violet, liq. colourless, but on standing bluish-violet.	F. made paler, and red col. extracted.	No action.	F. decolorised. (Resists this test better than other scarlets.)	Little or no action.	HNO_3 acts as with Croceïn Scarlet 7 B.
H. Fast Ponceau B. B. A. S. F.	F. violet, liqd. colourless. On standing, liq. becomes grn.-blue.	Fibre and sol. green.	F. dark blue-red, no col. extracted.	No action.	F. decolorised.	Little or no action.	HNO_3 gives a blue spot, which changes to red-brown with a blue or black border.

I. RED COLOURS—*continued.*

Colouring Matter.	HC	H_2SO_4	NaOH	NH_4OH	$SnCl_2$ and HCl	Alcohol.	Special Reactions and Remarks.
H. Scarlet 2 R. M. L. & B. (192).	F. not changed by cold acid, but on boiling nearly decolorised and much colour extracted.	Dil., no action. Concent. acid extracts the colour.	Nearly decolorised.	F. paler.	F. decolorised.	Little or no action.	HNO_3 gives violet spot, which afterwards changes to bright yellow.
H. Scarlet 3 R. M. L. & B. (197).	F. not changed even on boiling. Blue-red liqd. extracted.	No action.	Nearly decolorised.	Little effect.	F. deco l ed.	Little or no action.	HNO_3, as with Scarlet 2 R.
H. Claret Red B. M. L. & B.	F. little changed, liq. red.-violet.	F. at first violet, finally blue. Liquid at first colourless, afterwards bright blue.	F. orange-red, sol. yel.-red.	No action.	On heating, f. becomes almost colourless, or pale lilac.	Little or no action.	HNO_3 gives a violet spot, which afterwards becomes brownish with a faint blue border. Not affected so readily by HNO_3 as the Croceïn Scarlets are.
L. Carmoisin. F. Bayer & Co. (192).	Dil.: no action. Conc.: F. dark red-violet, liq. slightly lilac. On washing orig. colr. restored.	F. violet-black, liq. the same	F. somewhat brown, liqd. bright pink.	F. unchanged, liq. pink.	Slight action in cold; on boiling f. completely decolorised.	No action.	HNO_3: Brown-violet. Disappears on washing.
L. Primuline Red. B. S. & S. (210). Polychromine, Geigy & Co.	F. dark red-brown, liqd. slightly red-brown.	F. violet-blk., liq. dirty dark violet. On diluting, red.	F. dirty dark brown-red.	No action.	F. gradually changed to bright red-brown.	No action.	HNO_2: No action.
L. Orseillin B.B. Fr. Bayer & Co. (197).	F. first violet-blk., then blk.; soln. slight indigo blue.	F. blue-black, liqd. indigo-blue, on diln. reddish-violet.	F. violet, liqd. reddish-violet.	Like NaOH	F. slowly .. colrd. in the cold, rapidly upon boiling.	No action.	HNO_3: Violet spots, which disappear on washing.

I. RED COLOURS—*continued.*

Colouring Matter.	HCl	H_2SO_4	NaOH	NH_4OH	$SnCl_2$ and HCl	Alcohol.	Special Reactions and Remarks.
L. Congo Red. Act. Ges. Ber. (206).	Dilute: Fibre immediately blue-black. Conc.: Fibre blue-blk., liqd. colourless.	F. blue-black; on shaking up dissolves with a dark blue colr., on diln. remains blue-black.	F. scarcely changed, liq. colourless.	No action.	F. at first blue-black, then blue, afterwards grey, at last decolorised, all in the cold.	No action.	HNO_3: Blue-blk. spots NH_3 restores red. HNO_2: F. reddish-brn.; original colr. not restored by NH_3, but the f. is turned brownish-purple, and the liqd. blue-red.
L. Benzopurpurin 1 B. Fr. Bayer & Co. (207).	Dil.: F. red-brown, liqd. colourless. Conc.: Fibre dark brown.	F. blue-blk., liq. same; on diln., red-blk., then violet.	No action.	No action.	F. at first brn.-red, then pink, finally decolorised.	Slight extraction of colr.	HNO_2: F. brn.-blk. Picric acid: F. red-brown.
L. Benzopurpurin 11 B. Fr. Bayer & Co.	Dil.: F. bluish-blk., liq. colourless. Conc.: F. blue-blk.	F. blue-blk.; liq. dark-blue, on diln. blue.	No action.	No action.	F. at first blue-black, then clear grey, finally decolorised.	No action.	HNO_2: F. brn.-black, then more violet. Picric acid: F. dark brown.
L. Deltapurpurin G. Fr. Bayer & Co. (207).	Dil.: F. brn.-red, liq. colourless. Conc.: Fibre dirty grn.-blk.	F. blue-blk.: liq. dark blue; on diln. at first grey, then red-brn.	No action.	No action.	F. at first dark-brn. then brighter, later pink-red, finally decolorised.	No action.	HNO_2: F. violet-blk., turned violet-red with NH_3. Picric acid: F. brownish-red.
L. Deltapurpurin 5 B. Fr. Bayer & Co. (207).	Dil.: F. red-brn. Conc.: F. olive-blk.	F. dark olive-brn.; liqd. dirty green; on diln. red-brown.	No action.	No action.	F. at first cinnamon brn., then gradually decolorised in the cold.	Some colr. extracted.	
L. Brilliant Congo. Fr. Bayer & Co. (204).	Dil.: F. brn.-red, liq. colourless. Conc.: F. violet-blk.	F. blue-blk.; liq. blue, on diln. purple-violet.	No action.	No action.	F. at first red-brn., then decolorised.	Slight extraction of colr.	HNO_2: F. blk., turned violet-blk. by NH_3. Picric acid: F. brownish.

1. RED COLOURS—*continued.*

Colouring Matter.	HCl	H_2SO_4	NaOH	NH_4OH	$SnCl_2$ and HCl	Alcohol.	Special Reactions and Remarks.
L. Rosazurin B. Fr. Bayer & Co. (204).	Dil.: F. dark purple-red. Conc.: Fibre olive-green.	F. dark blue; liq. dark blue; on diln. first greenish, then red-violet.	No action.	No action.	F. at first dark purple-red, then decolorised.	Extracts some dye with magenta-red colour.	HNO_2: F. dark yellow-grey, on washing and moistening with NH_3 red-brown.
L. Congo Corinth. Fr. Bayer & Co. (204).	Dil.: F. black. Conc. acid: F. black.	F. black, liqd. dark blue; on diln. remains blue.	F. much redder; liq. colourless; on washing orig. colour is restored.	F. redder, liqd. slightly pink.	F. at first blk., then blue-grey, and finally decolorised.	Liqd. a slight pink.	HNO_2: F. dark blue-black; washing with NH_3 f. becomes magenta-red.
L. Hessian Purple B. Leonhardt & Co. (204).	Conc.: F. dark grey, almost black.	F. grey-black, liqd. slightly blue.	No action; liq. slightly pink.	Liqd. slightly pink.	F. at first reddish-grey, then decolorised.	No action.	HNO_2: F. dark purple-violet, with NH_3 dark brown.
L. Hessian Purple N. Leonhardt & Co. (204).	Dil.: F. black, liqd. colourless.	F. black, liqd. blue; on diln. grey-blue.	No action.	No action.	F. at first blk., then decolorised.	Liqd. scarcely coloured.	HNO_2: F. violet-blk., changed by NH_3 to dark red-brown.
L. Azarine S. M. L. & Br. (209).	F. gradually dark brn.-red. liq. scarcely coloured. On diln., original colr. restored.	F. darker, liqd. beautiful red. On diln. f. and liqd. become yellow.	F. bluer red, soln. bright cherry-red.	Action similar, but slighter than NaOH	On boiling the f. and liq. become yellow.	Liqd. slightly coloured pink.	Picric acid: F. brown. The material smells strongly of turkey-red oil, and ash contains Sn. HNO_2: No action. HNO_3: Orange-red spot. On adding NH_3 to yellow soln. obtained with $SnCl_2$ and HCl, and liq. become violet.
L. Azoeosin. Fr. Bayer & Co. (174).	F. dark red violet, liqd. slightly lilac. On diln. orig. colr. restored.	As with HCl	F. dirty orange.	F. scarlet-red, liqd. scarcely coloured.	In the cold only very slight action; on heating the f. is incompletely decolorised. Liqd. colourless.	No action.	HNO_3: Brown spot, disappears on washing.

I. RED COLOURS—*continued.*

Colouring Matter.	HCl	H_2SO_4	NaOH	NH_4OH	$SnCl_2$ and HCl	Alcohol.	Special Reactions and Remarks.
H. Alizarin (280).	Dil., no action; concent., f. bright yellow, liqd. amber-yellow.	Dil., no action; concent., red colour extracted.	F. and solution violet.	No action.	F. orange-yel., liqd. bright yellow.	No action.	Gives no fluorst. soln. on boiling with $Al_2(SO_4)_3$ (distinction from madder and purpurin). Boiled with $Ba(OH)_2$ solution, fibre becomes violet.
L. Alizarin S (267).	F. orange-yellow, liqd. bright orange.	F. orange-brn., liq. orange. On diln. yel.	F. violet, liq. also violet.	F. violet-red, liqd. colourless.	F. gradually becomes orange, liq. yel. (in the cold).	No action.	The yellow with $SnCl_2$ and HCl is turned violet by NaOH. Ash contains Al or Cr
L. Alizarin S. Maroon with $K_2Cr_2O_7$ (267).	F. brn.-yellow, liqd. yellow.	F. brown, liqd. bright brown-red. On diln. yellowish.	F. violet; liq. violet.	No action.	In the cold no visible action. On heating f. brn.-red, liq. slightly brn.-red.	No action.	HNO_3: Orange-yellow spot. Ash contains Cr
H. Purpurin (270).	Boiled with dil. acid, fibre orange-yellow and liquid yellow.	As with HCl.	Heated with dil. soda, f. and liq. cherry-red.	Boiled with dil. NH_4OH liq. pale pink, f. not changed.	F. brown-red, liqd. amber-yellow.	Solution red.	$Ba(OH)_2$ turns f. cherry-red and extracts a pale bluish-red soln. Boiling with aluminium sulphate and cooling, gives an orange fluorescent solution.
H. Madder (277).	F. brown-red.	F. brownish-red, solution red.	F. and solution purple.	Wool brn.-red, cotton not changed.	Little colour extracted.	No action.	Nitric acid colours f. bright yellow.
H. Orchil or Archil (320).	F. little changed, solution red.	F. and soln. purple, afterwards brown.	F. bluish-purple.	As with NaOH	At once decolorised.	Bluish-red solution.	Ash usually contains Al
H. Peachwood, Brazilwood (333).	F. dark red, soln. pink.	F. brn., soln. yellow changing to brown.	Much colr. extracted, blue-red. Cotton almost decolorised.	As with NaOH	F. and solution bluish-red on heating.	Pale yellow solution.	Nitric acid colours fibre brown-yellow. Boiling soap solution removes much colour, solution bluish-red.
H. Barwood (326).	No action.	F. red-brown, solution dirty brown.	F. purplish, solution colourless.	As with NaOH	F. unchanged, solution red.	Red solution.	Nitric acid colours wool dark olive.

I. RED COLOURS—*continued.*

Colouring Matter.	HCl	H_2SO_4	NaOH	NH_4OH	$SnCl_2$ and HCl	Alcohol.	Special Reactions and Remarks.
H. Sanderswood (335).	No action.	F. and soln. reddish-brn.	F. purplish, solution colourless.	As with NaOH	Fibre unchanged, solution red.	Red solution.	Nitric acid colours wool dark olive. Boiled with $FeSO_4$ colour becomes violet.
H. Safflower (338).	Cotton decolorised.	Cotton decolorised.	With dilute NaOH, cotton pale yellow.	Cotton, flesh-colour.	Cotton straw yellow.	No action.	
H. Cochineal.	F. orange-red, soln. orange-pink.	F. and solution bright pink.	Solution purple.	As with NaOH	F. and solution orange-red.	No action.	Nitric acid colours fibre yellow.
Ammoniacal Cochineal.	Less affected than ordinary cochineal.	Fibre yellow-brown.	Becomes bluer.	Gradually violet.	...	...	Ash contains Al
II. VIOLET COLOURS.							
H. Galleïn (73).	F. brown-red, liqd. amber-yellow.	As with HCl or orange.	Paler or bluer.	No action, or becomes paler.	Fibre crimson, liquid red.	No action.	HNO_3 gives a bright yellow spot. Bleaching-powder solution has no action. Ash usually contains Cr.
L. Fast Violet.	F. dark blue-black; liqd. slightly blue.	F. black, liqd. grey-blue. On dilution first green-blue, then red. F. again violet.	F. blue-black, liqd. slightly violet.	F. unchanged; liqd. slightly violet.	Decolorised gradually in the cold, rapidly on boiling.	Very slightly coloured violet.	HNO_3 : Blue-black spot.
L. Azo-Violet (203).	Dil.: F. blue. Conc.: Fibre blue-blk.; liq. colourless.	F. blue-black, liq. blue-grn.	Fibre crimson-red; liquid colourless.	F. dark violet; liqd. slightly magenta-red.	Decolorised only slowly.	No action.	Picric acid: F. black. Dilute acetic acid changes violet to blue.
L. Hessian Violet (204).	F. dark blue, liqd. scarcely coloured.	F. dark violet-blue, liquid blue-blk.; on dilution blue-violet.	F. redder; liq. colourless.	F. redder, liq. slightly reddish-violet.	Fibre at first beautiful blue; decolorised by continued boiling.	No action.	HNO_3 : F. becomes dirty grey-violet, changed to dirty crimson-red by NaOH. HNO_3 : Large spot with blue rim.

II. VIOLET COLOURS—*continued.*

Colouring Matter.	HCl	H_2SO_4	NaOH	NH_4OH	$SnCl_2$ and HCl	Alcohol.	Special Reactions and Remarks.
L. Heliotrope (203).	Dil.: F. dark violet. Con. F. blue-blk., liquid bright blue; on dilution violet.	F. blue-black; liqd. blue.	F. dark crimson-red; liq. colourless.	No particular action.	F. at first dark grey, then decolorised.	No action.	HNO_2: F. becomes greenish-grey; on washing and treating with NH_3 is changed to brown-orange; liq. slightly-brownish. Picric acid: F. dark brown.
H. Methyl-Violet (234).	F. yel.-brown, liquid amber-yellow; violet colr. restored on dilution.	As with HCl	F. at first pale red - violet, afterwards decolorised.	F. pale lilac, nearly decolorised.	F. green, but nearly decolorised on standing, liq. yellowish-grn.	Colour extracted.	
H. Phenyl-Violet, or Spirit-Violet (235).	F. dark green, soln. brownish.	F. and soln. red-brown.	Decolorised.	Decolorised.	Blue colr. extracted; only decolorises slowly.	Colour extracted.	HNO_3 gives a green spot.
H. Benzyl-Violet (237).	F. yel.-brown, liquid amber-yellow; violet colr. restored on dilution.	As with HCl	Fibre at first bluer, afterwards decolorised.	Almost decolorised, fibre pale bluish-lavender.	F. bright grn., liq. pale yel.	Colour extracted.	
L. Acid Violet 7 B. F. Bayer & Co. (234).	F. green, liq. yellow-brn.; on diln. grn.-blue.	Fibre at first blackish, then brown, then brn.-red; liq. brn.-red; on diln. greenish-blue.	F. immediately decolorised; liquid colourless.	As with soda.	F. beautiful green; liquid blue-green. On diln. fibre and liq. both blue.	Liq. scarcely coloured violet.	HNO_2: No action. HNO_3 First olive-green, then dirty yellow spots. On washing remains unchanged.
H. Perkin's Purple (257).	F. unchanged, solution blue-pink.	Little or no action.	F. blue, colr. restored on washing.	No action.	F. dirty brn., but not decolorised.	Colour extracted.	HNO_3 has no effect. Cl bleaches the colour slowly.
L. Gallocyanin D. & H. (276).	F. violet; liqd. beautiful violet.	F. dark blue-black, liquid intense Berlin blue; on dilution bright magenta-red.	F. violet blk.; liquid dirty purple violet.	As with soda, only rather slighter action.	F. in the cold becomes yellowish-grey; liquid colourless.	No action.	HNO_3: F. dirty grey-violet; liq. at first blue-green, then green, and finally yellow.

II. VIOLET COLOURS—*continued.*

Colouring Matter.	HCl	H_2SO_4	NaOH	NH_4OH	$SnCl_2$ and HCl	Alcohol.	Special Reactions and Remarks.
L. Muscarin. D. & H. (260).	F blue-blk.; liquid dirty blue.	F. greenish-black, liquid greenish; on dilution dirty violet.	F. brn.-black; liqd. scarcely coloured.	F. violet-blue; liqd. scarcely violet.	F. blackish; on heating blue, then green, and finally yellowish-grey.	No action.	HNO_3: Black spot.
H. Alizarin (279).	F. and liquid dull yellow.	As with HCl	Colour of fibre bluer.	No action.	As with HCl	No action.	Destroy the colour by boiling with dilute HCl, wash and add NaOH; the alizarin remaining on the fibre is dissolved with purple colour.

III. BLUE COLOURS.

Colouring Matter.	HCl	H_2SO_4	NaOH	NH_4OH	$SnCl_2$ and HCl	Alcohol.	Special Reactions and Remarks.
H. Resorcin Blue (159).	...	Dil., no action.	Solution blue, with red fluorescence.	As with NaOH			
L. Benzo-azurine G. Fr. Bayer & Co. (208).	F. blue-black, liqd. colourless.	F. blue-black, liq. greenish-blue. On dil. more of reddish blue.	F. dark carminoisin red, liqd. slightly pink.	F. dark violet, liq. slightly cherry-red.	Decolorised only gradually.	No action.	By boiling with soap solution liq. coloured strongly blue.
L. Azo-blue. Fr. Bayer & Co. (208).	Dil.: No action. Conc.: F. blue-blk., liqd. colourless.	F. blue-black, liqd. blue.	F. cherry-red, liqd. slightly pink.	F. dark violet-red, liq. pinky red.	F. first blue-black, then gradually decolorised.	No action.	Picric acid: F. blackish-brown.
H. Soluble Blue. B. S. & S. (229).	Extracts blue colour.	F. and liq. red-brown.	Fibre reddish-brown.	Decolorised at once.	F. little changed, blue, colour extracted.	Absolute alcohol, even on boiling, extracts no colr.	HNO_3 gives dark spot, which changes to dark green with black border.

III. BLUE COLOURS—*continued.*

Colouring Matter.	HCl	H_2SO_4	NaOH	NH_4OH	$SnCl_2$ and HCl	Alcohol.	Special Reactions and Remarks.
H. Spirit Blue. A. Poirrier (228).	F. dark green, soln. brownish.	F. and solution reddish-brn.	F. brick-red.	Decolorised slowly.	F. not changed, liq. colourless.	*Absolute* alcohol extracts colr., even in the cold.	HNO_3 gives black spot, which changes to dark green.
H. Alkali Blue 3 B. B. A. S. F. (230).	F. greenish blue, solution almost colourless.	F. and liquid red.-brown on standing.	F. at first red.-brown, afterwards decolorised.	Decolorised rapidly.	F. not changed, liq. colourless.	*Absolute* alcohol extracts colour, even in the cold.	HNO_3 gives light green spot with black border.
L. Victoria Blue. B. A. S. F. (232).	F. at first blue-black, liq. reddish or yellow-brn. On diln. fibre becomes first grn., then blue again.	As with HCl, or orange.	F. dark brown-red or silver-grey, liq. colourless.	F. blue-black, decolorised or slightly grn., liq. colourless.	In the cold f. dark blue, on boiling grn.-blue. Liq. in the warm grnish., upon cooling bright blue.	Some colour extracted cold; on boiling copious extraction.	HNO_3: At first black spots which gradually becomes reddish-brown. NH_3 turns brown-yellow; the last colr. remains after washing.
H. Indulines (250).	F. violet, liqd. deep blue.	Solution dark blue.	Reddish-violet colr. abstracted, the soln. decolorised on addition zinc powder. Violet colour restored by exposing filtered soln. to air.	As with NaOH	Extracts violet or green colr.	Blue-violet colour extracted.	Induline NN is not changed by bleaching-powder solution. It changes some indulines to reddish-grey, whilst others are decolorised. HNO_3 gives dark bluish-green spot.
L. Basle Blue. D. & H. (282).	F. dark grey, liqd. yellow. On dil. becomes blue again.	F. at first blue-black, then green, and at last yellowish; liq. yel. On diln. both become blue again.	Fibre darker.	No action.	No action.	Liquid very slightly blue.	HNO_3: Black spot.
H. Indophenol Blue (259).	F. greyish-brn.	F. greyish-brn.	No action.	No action.	Decolorised.	Blue colour extracted.	Boiled with olive oil purplish colour is extracted.

III. BLUE COLOURS—*continued.*

Colouring Matter.	HCl	H_2SO_4	NaOH	NH_4OH	$SnCl_2$ and HCl	Alcohol.	Special Reactions and Remarks.
H. Vat Indigo-blue (313).	No action.	Dil., no action; concent., blue solution.	No action.	No action.	On heating f. becomes paler, soln. greenish-yellow.	Boiling absolute alcohol gives blue soln., on standing becoming colourless with separation of indigotin.	Chloroform extracts blue colr. Strong HNO_3 gives bright yellow spot. Indigo-dyed cotton if burnt gives off purple vapour, which can be condensed on a cold porcelain as a blue spot. Presence of traces of Fe or Zn in ash will indicate nature of reducing agent used in vat.
H. Indigo-carmine (313).	Little action, or soln. grn.-blue.	Soln. violet-blue.	F. greenish. On boiling with dilute NaOH colour abstracted, soln. yellowish-brn., but becomes blue on acidifying.	As with soda (or little action).	Fibre decolorised on heating.	Little or no colour extracted.	Colour extracted by boiling with dilute Na_2CO_3; silk or wool may be dyed in the acidified solution. Nitric acid gives yellow spot. No indigotin vapours on heating.
H. Logwood Blue (332).	Fibre red or brown, soln. red.	As with HCl	F. and soln. purple.	As with NaOH	Fibre and soln. at first red, afterwards brown.	No action.	If used for topping vat indigo-blue, the logwood dye can be removed by boiling with dilute HCl, while the indigo is unaffected thereby.
H. Prussian Blue.	No action.	No action (yel.-brown or paler).	F. brown on heating.	No action (or as with soda).	No action.	No action.	Ash contains iron. Concentrated HNO_3 gives green spot. Boiled with NaOH, solution contains ferrocyanide, and on acidifying filtrate and adding Fe_2Cl_6 blue precipitate is obtained.
H. Ultramarine Blue (inorganic).	Decolorised.	Decolorised.	No action.	No action.	Decolorised.	No action.	On burning fibre blue-coloured ash remains. Only met with on calico or woollen prints.

III. BLUE COLOURS—*continued.*

Colouring Matter.	HCl	H_2SO_4	NaOH	NH_4OH	$SnCl_2$ and HCl	Alcohol.	Special Reactions and Remarks.
L. Meldola's Blue. New blue. Cassella & Co. (260).	F. red-blue.	F. dark grey, liqd. grey.	F. brownish violet, liqd. slight pink-red.	As with NaOH	F. at first grn., then almost decolorised; liq. colourless, quickly greenish again in air, then blue.	Liquid very slightly blue.	
L. Naphthalene Blue G. Fr. Bayer & Co. (260).	F. brownish-violet; liqd. brn.-orange.	F. brown-blk.; liq. dark-brn. On diln. dirty blue.	F. brown; liq. brn.-orange.	F. brownish-violet; liqd. bright reddish brown.	F. discoloured; liq. colourless.	Liquid very slightly violet.	HCl gas is sufficient to change the colour of f. to chocolate-brown.
L. Nile Blue. B. A. S. F. (260).	F. at first greenish, then orange-yellow, liqd. orange-yellow.	F. and liqd. brn.-red. On diln. at first yellow, then green, finally blue again.	F. red, liquid pink.	Fibre violet.	F. at first green, then decolorised; liq. colourless, becomes greenish-blue in the air.	L. very slightly blue.	HNO_3: First yellow spot, becoming green in middle and at the rim yellow.
H. Alizarin Blue. B. A. S. F. (269).	(Little action, or) F. violet, liq. yellowish-red.	Dil.: f. violet, liqd. slightly red. Conc., (little action, or) violet liqd.	F. bluish-green (and paler).	No action (or gradual paling).	F. at first violet, on heating brownish-red, liq. brn.	No action.	HNO_3 gives a bright yellow spot, gradually turning to brown. Soap and bleaching powder no action. Phosphoric acid gives orange-red soln., which on diluting and adding NH_4OH becomes blue. Dilute ammoniacal alcoholic soln. shows characteristic absorption-bands. Ash usually contains Cr.
H. Methylene Blue. B. A S. F. (287).	F. nearly decolorised, soln. blue-green.	F. and liquid green.	F. blue-violet.	No action.	Decolorised.	Greenish-blue colour extracted.	HNO_3 give green spot, which does not change further. Bleaching powder solution turns it first green, and gradually decolorises it.

IV. GREEN COLOURS.

Colouring Matter.	HCl	H_2SO_4	NaOH	NH_4OH	$SnCl_2$ and HCl	Alcohol.	Special Reactions and Remarks.
H. Cœrulein. B. A. S. F. (73.)	F. duller grn., liquid claret-red.	As with HCl, liquid dirty amber - yellow (or dull red).	No action (or paler).	No action (or paler).	F. brown.-red, liq. brn.: on washing with water colr. gradually restored.	No action.	HNO_3 gives a brown spot.
L. Resorcin Green. D. & H. (158).	F. grey-yellow, liqd. orange-red.	F. bright brn., liq. the same. On diln. no change.	F. slightly darker, liq. greenish.	No action.	Slightly decolorised, liqd. brownish.	No action.	HNO_3: Yellow brown spot. Ash contains iron.
H. Acid Green. (238).	F. pale green.	F. brown, liq. yellow.	Decolorised.	Decolorised.	F. almost decolorised, liq. yellow.	Green colour readily extracted.	
H. Alkali Green.	F. dark olive-green, soln. red.-brown.	F. and soln. dark brown.	Decolorised.	Decolorised.	F. not changed, bluish-green colour extracted.	Green colour extracted.	
H. Methyl Green B. A. S. F. (240).	F. and liqd. pale yellow; colr. restored on washing.	Fibre much bleached, liq. colourless.	Decolorised.	Decolorised.	F. almost decolorised, liq. yellow.	Blue-green colour extracted.	Heated to 100° C. becomes blue-violet. (Distinction from Malachite Green.)
H. Malachite Green (241).	F. and liquid bright orange; on washing grn. colr. restored.	Fibre much bleached, liq. bright orange.	Decolorised.	Decolorised.	F. almost decolorised, liq. yellow.	Green colour extracted.	Heated to 100° C. colour does not change to blue-violet. (Distinction from Methyl Green.)
H. Helvetia Green (242).	Liqd. yellow; green colour restored on dilution.	Decolorised.	F. buff-yellow.	As with NaOH	Almost completely decolorised.	Bluish-green colour extracted.	
H. Aldehyde Green (287).	F. bright yellow.	F. orange.	Little action, f. afterwards paler.	At first little action, afterwards bleached.	Slowly decolorised.	Green colour extracted.	HNO_3 gives a brown spot.

IV. GREEN COLOURS—*continued.*

Colouring Matter.	HCl	H_2SO_4	NaOH	NH_4OH	$SnCl_2$ and HCl	Alcohol.	Special Reactions and Remarks.
H. Vat Indigo and Old Fustic (345).	F. paler, liqd. blue.	As with HCl	F. greenish-blue, liq. yellow.	F. paler or blue, liq. yellow or greenish.	F. much paler, liquid green-yellow.	See Indigo.	Boiling glacial acetic acid gives green soln.; on diluting with water blue is precipitated. Boiling $Al_2(SO_4)_3$ gives yellow soln. with green fluorescence. Remove yellow colr. by boiling dilute Na_2CO_3, and test the blue remaining for indigo.
H. Vat Indigo and Lead Chromate (212).	Yellow removed at once, blue afterwards; liq. dull yellow.	F. dirty yellowish-green.	Yellow removed; liqd. pale yellow.	No action.	F. at first blue, afterwards decolorised.	See Indigo.	Ash contains Pb and Cr. Blackened by NH_4HS. Bleaching powder soln. changes colour to yellow.
H. Indigo Carmine and Picric Acid (313).	F. at first blue, afterwards very pale; liq. blue.	As with HCl	F. almost decolorised, liq. pale yellow.	As with NaOH	Decolorised.	...	Cold water extracts Picric Acid; test soln. with KCN.
H. Chrome Green (Inorganic).	No action.	No action.	No action.	No action.	No action.	No action.	Boiled with soln. bleaching powder gives yellow liq. containing chromate. Occurs only on calico prints.
V. YELLOW COLOURS.							
H. Picric Acid (142).	Colr. extracted on boiling, liqd. grn-yel.	Decolorised.	Fibre becomes orange, soln. yellow.	Fibre becomes paler, yellow colr. extracted on boiling.	F. bleached, the liqd. colourless.	Yellow colr. extracted.	Heated with KCN soln. fibre becomes red. In compound colrs. cloth should be extracted with alcohol, and soln. tested for picric acid with KCN.
H. Victoria Yellow (152).	Decolorised, washing restores colour.	...	...	No change.	...	...	Warm water extracts the colr.

V. YELLOW COLOURS—*continued.*

Colouring Matter.	HCl	H_2SO_4	NaOH	NH_4OH	$SnCl_2$ and HCl	Alcohol.	Special Reactions and Remarks.
H. Naphthol Yellow (154).	Decolorised almost completely.	As with HCl	Fibre orange (and gradually paler), soln. yellow.	F. (unchanged or) paler, yel. colr. extracted on boiling.	F. bleached, the liquid colourless.	Yellow colour extracted.	Water extracts colour, and the yellow soln. is decolorised by H_2SO_4. Boiling KCN extracts a red colour. Wrapped in white paper and heated to 120° C., leaves a stain on paper.
H. Naphthol Yellow S (156).	Fibre (slowly) bleached, soln. colourless.	Decolorised.	F. paler (or decolorised), liq. yellow.	Fibre little changed, liq. pale yellow.	Bleached.	No action.	Boiling water extracts nothing. Heated to 128° C. in white paper, leaves no stain.
H. Aurantia (156).	Fibre pale yel.	F. yellow-drab.	Little or no effect.	No action.	F. brown on heating.	Colr. readily extracted.	Heated with $SnCl_2$ gives dark brown-red colour, afterwards decolorised.
L. Quinoline Yellow. B. A. S. F. (174).	F. yellow, liq. colrless. On diln. original pale yellow restored.	As with HCl	Fibre at first deeper yellow, then gradually decolorised; yellow colr. restored on washing.	Almost without action.	In the cold no action. On heating yel., f. somewhat paler.	No action.	HNO_3 gives a deep yellow spot, probably only due to the action of the HNO_3 upon the wool.
H. Chrysoïdine. B. S. & S. (179).	Fibre red.	Yellow colour extracted.	F. paler and yellower.	F. yellower.	Almost decolorised.	Yellow colr. extracted.	
H. Fast Yellow. B. A. S. F. (187).	Red.	F. brown- or yellow-red, liquid red.	(Little action; or) soln. brn.-yellow.	Little action.	F. bright red, afterwards decolorised.	A little colr. extracted.	HNO_3 gives a bright red spot.
H. Orange II. A. Poirrier (186).	Fibre and liq. blue-red.	As with HCl, but bluer.	F. deep red.	No action.	Completely bleached.	No action.	
H. Orange III. F. Bayer & Co. (188).	F. red, liquid pink.	F. and liquid bright blue-red.	Fibre dull yellowish-red.	F. not changed, liquid slightly yellow.	Completely bleached.	A little colr. extracted.	
H. Orange IV. A. Poirrier (184).	F. red-violet, liqd. violet.	As with HCl	No action.	F. not changed, liqd. yellow.	At first f. becomes deep violet on heating, gradually lighter and finally bleached	Yellow colour extracted.	

V. YELLOW COLOURS—*continued.*

Colouring Matter.	HCl	H_2SO_4	NaOH	NH_4OH	$SnCl_2$ and HCl	Alcohol.	Special Reactions and Remarks.
L. Citronin. Geber & Uhlmann (156?).	F. dark red-violet. On diln., red-violet liquid becomes magenta-red.	F. dark violet, liquid violet.	F. dirty greenish-yel., soln. colourless. Becomes yel. on dilution.	F. unchanged, liquid colourless.	F. at first yel.-brn., on heating decolorised; liquid slightly yellowish.	Slightly extracted.	HNO_3: At first red-violet spot, becoming magenta-red in middle, and violet at the rim.
L. Croceïn Orange. Fr. Bayer & Co. (184).	F. red-brown, liq. pink-red.	F. darker, liq. orange. On washing the fibre becomes orange again.	F. orange-brn., liquid very slightly coloured.	No action.	Almost without action in the cold, and boiling quickly and completely decolorised.	No action, or only very slight orange-red colour.	HNO_3: Blue-blk. spot. Bleaching powder: Fibre brownish, then decolorised.
L. Chrysamine. Fr. Bayer & Co. (206).	Dil. acid pale yellow. Conc. acid, f. red-brown, liqd. bright pink. On diln. yel.	F. magenta-red, liq. red-violet.	Fibre dark orange, liqd. scarcely coloured.	Fibre bright orange, liq. colourless.	F. at first dirty yellow, gradually decolorised.	No action.	HNO_3: Brown spot gradually becoming red-grey.
L. Hessian Yellow. Leonhardt & Co. Fr. Bayer & Co. (204).	Dil. acid: F. brighter. Conc. acid: F. blue-blk., liq. violet.	F. dark violet, liq. red-violet.	F. beautiful dark red, liq. bright pink.	F. dark orange, liqd. slightly orange-red.	F. at first pale yellow, gradually completely decolorised.	No action.	HNO_3: Brownish spot with bright yellow rim. HNO_2: Acts like dil. HCl.
L. Brilliant Yellow. Leonhardt & Co. Fr. Bayer & Co. (208).	Dil. acid: No action. Conc. acid: F. dark violet, liquid slightly colrd.	F. violet-blk., liquid violet.	F. cherry-red, liqd. slightly pink.	As with NaOH	F. at first dirty yel., quickly completely decolorised.	No action.	
L. Chrysophenine. Fr. Bayer & Co. (208).	Dil. acid: No action. Conc. acid: Fibre violet-black, liqd. scarcely coloured.	F. brown, then dark red-violet. On diln. blue.	F. unchanged, liq. slightly yellowish.	No action.	Fibre at first brn.-yellow, then decolorised.	No action.	HNO_2: No action. HNO_3: Violet spot.

V. YELLOW COLOURS—*continued.*

Colouring Matter.	HCl	H_2SO_4	NaOH	NH_4OH	$SnCl_2$ and HCl	Alcohol.	Special Reactions and Remarks.
L. Primulin Yellow. Brook, Simpson, & Spiller (209).	No noticeable action.	Fibre at first brighter and darker yellow, then pale yel.	Fibre rather brighter and orange-yellow, liquid colourless.	No action.	Slight action.	No action.	HNO_2: The f. becomes rather dark orange; treated with NH_3 turns orange-brown. (Primulin is a derivative of thio-toluidine, and contains $C_{28}H_{17}(SO_3Na)N_4S_3$).
L. Toluylene Orange G. K. Oehler & Co	Dil.: No action. Conc.: F. violet, liq. reddish. On diln. f. and liquid regain original colr.	F. magenta-red, liqd. not strongly coloured.	Fibre bright orange-red, liqd. slightly coloured.	No action.	Fibre at first more pink-red, on boiling decolorised, liquid colourless.	No action.	HNO_3: F. becomes grey; the grey colr. treated with NH_3 turns dirty yellow.
L. Toluylene Orange R. K. Oehler & Co.	Dil.: F. more pink-red. Conc.: F. paler, liqd. yellow. On diln. soln. becomes flesh colour, the f. pink-red.	F. yellowish, liq. yellow.	Fibre more orange-red, liqd. colourless.	No action.	F. at first pink-red, becomes decolorised on boiling rather slowly.	No action	HNO_2: Fibre becomes greyish-lilac; treated with HN_3 changes to reddish-grey. HNO_3: Dirty reddish-violet spots, gradually becoming grey.
L. Primulin Orange. Brook, Simpson, & Spiller (209).	F. red-brown, liq. also red-brown.	Fibre orange-brn., liq. dark red.	F. dark red-brown, liquid slightly coloured.	No action.	Fibre at first orange-brn., then decolorised.	Colour somewhat extracted.	HNO_3: Red-brown spot.
L. Oriol. J. R. Geigy & Co.	Dil.: No action. Conc.: F. dark red, liquid bright red. On diln. again yellow.	As with HCl.	F. orange-red, liquid colourless.	F. orange-yel., liq. scarcely coloured.	F. at first light yellow, then gradually decolorised; liq. colourless.	No action.	HNO_2: No action. HNO_3: light orange-red spot. The colouring matter is distinguished by its remarkable fastness to light.
L. Auramine. B. A. S. F. (244).	F. almost decolorised, liq. colrless. On diln. yel. partly restored.	F. decolorised, liquid colourless.	F. decolorised, liq. colourless. On washing yel. colr. partly restored.	F. paler, liqd. colourless.	Gradually decolorised in the cold, on heating very rapidly.	No action.	HNO_3 gives a colourless white spot, which gradually turns orange in the middle, leaving a white rim (compare Quinoline Yellow).

V. YELLOW COLOURS—*continued.*

Colouring Matter.	HCl	H_2SO_4	NaOH	NH_4OH	$SnCl_2$ and HCl	Alcohol.	Special Reactions and Remarks.
L. Curcumin W. Act.-Ges. Berlin. Leonhardt & Co. (288?).	Dil.: No action. Conc.: F. violet-blk., liq. slightly coloured.	F. violet-blk., liq. beautiful violet. On diln. blue.	As with brilliant yellow.	As with brilliant yellow.	Fibre at first brn.-yellow, then decolorised.	No action.	
H. Phosphine (246).	F. nearly decolorised, soln. yellow.	Soln. green-yellow.	Fibre becomes paler and yellower.	Fibre becomes paler, a bright yellow.	F. nearly decolorised.	A little colour extracted.	
L. Tartrazin. B. A. S. F. (288).	Fibre more orange, liqd. yellow.	As HCl	Fibre more orange, liqd. orange-yel.	As NaOH, only slighter.	Upon heating decolorised.	No action.	HNO_3: No action.
H. Nitro-alizarin (267).	F. pale straw yellow, soln. yellow.	F. brn.-yel. (or decolorised), liq. yellow.	F. claret-red or brownish, liquid colourless.	Cold, no action; hot, as with NaOH, but f. not so dark.	F. deep yellow, liq. yellow.	No action.	HNO_3 gives bright yellow spot. Boiling $Ba(OH)_2$ colours fibre claret-red. Ash usually contains Cr
L. Galloflavin. B. A. S. F. (276).	Fibre rather darker, liquid yellow. On diln. f. and liquid almost colourless.	As with HCl	Fibre rather darker and more orange-yellow, liquid yellow.	F. darker and slightly olive-grn., liqd. almost colourless.	No particular action.	...	Warmed with Fe_2Cl_6, fibre becomes dirty olive-green. Yarn dyed with alum, tartar, and $SnCl_2$ (276).
H. Madder (279).	Little action.	F. brown-red, soln. red.	F. and soln. purple.	Fibre brown.	F. unchanged, solution pale red.	No action.	Heated with $FeCl_6$ fibre becomes olive-brown.
H. Quercitron Bark (343).	F. little affected, soln. yel.	F. brown-yel., soln. yellow.	F. little changed, soln. yel.	F. unchanged, soln. yellow.	F. little affected, soln. yel.	No action.	With HNO_3 fibre light blue. Heated with Fe_2Cl_6 fibre becomes olive. Becomes orange by boiling with lead acetate.
H. Flavin (342).	F. and soln. yellow.	F. and soln. yellow.	F. and soln. yellow.	F. little affected, soln. yel.	F. brown-yel., soln. bright yellow.	No action.	With HNO_3 fibre dark brown. Heated with Fe_2Cl_6 fibre becomes olive. Boiling acetic acid gives yellow soln. with green fluorescence. Becomes orange by boiling with lead acetate.

V. YELLOW COLOURS—*continued.*

Colouring Matter.	HCl	H_2SO_4	NaOH	NH_4OH	$SnCl_2$ and HCl	Alcohol.	Special Reactions and Remarks.
H. Old Fustic (343).	F. and soln. orange (or decolorised).	F. and soln. brn. (or little changed).	Fibre little changed.	F. unchanged, soln. yellow.	F. orange, soln. colourless.	No action.	With HNO_3 fibre pale yellow. Heated with Fe_2Cl_6 fibre becomes olive. Boiled with acetate of alumina gives yellow soln. with bluish-green fluorescence. Ash usually contains Al.
H. Young Fustic (345).	F. unchanged, solution pale yellow.	F. and soln. red-brown.	F. red-brown.	As with NaOH	No action.	No action.	With HNO_3 fibre dark brown. Heated with Fe_2Cl_6 fibre becomes olive.
H. Weld (347).	F. little affected, soln. pale yellow.	F. brown-yel.	F. little affected, soln. pale yellow.	No action.	Fibre little affected.	No action.	HNO_3 no action. Heated with Fe_2Cl_6 fibre becomes olive. Colour unchanged by boiling with lead acetate.
H. Persian Berries (348).	F. unchanged, soln. yellow.	Fibre orange-brown, soln. grn.-yellow.	F. unchanged, soln. brownish-yellow.	Colour slightly extracted.	Fibre brown, soln. yellow.	No action.	With HNO_3 fibre brown. Heated with Fe_2Cl_6 fibre becomes olive. Becomes orange by boiling with lead acetate.
H. Annatto (352).	Little affected, or brownish-red.	Fibre and solution blue.	Little affected.	As with NaOH	Decolorised.	Solution bright yellow.	Dyed blue with K_3FeCy_6+HCl
H. Turmeric (357).	Fibre reddish-brown, soln. colourless.	Fibre reddish-brown, solution brown.	Fibre bright reddish-brn., soln. orange-brown.	Fibre bright reddish-brn., soln. orange.	Fibre reddish-brown, soln. colourless.	Colour extracted, solution orange or yellow with grn. fluorescence.	With HNO_3 fibre pale yellow. Boracic acid added to HCl and alcoholic soln. gives bright red colour. Ash usually contains Al.
H. Iron Buff.	Fibre straw-yellow or decolorised.	Little action.	No action.	No action.	Decolorised	No action.	Fibre blackened with ammonium sulphide or H_2S.
H. Chrome Yellow.	Fibre decolorised, solution pale yellow.	Fibre greenish-yellow or dull yellow.	Fibre redder or paler, liq. pale yellow.	Little action.	Decolorised.	No action.	Blackened by H_2S. Reddened or stripped by NaHO; solution yellow.

VI. BROWN COLOURS.

Colouring Matter.	HCl	H_2SO_4	NaOH	NH_4OH	$SnCl_2$ and HCl	Alcohol.	Special Reactions and Remarks.
H. Catechu Brown (104).	Little or no change, soln. pale orange.	Little or no change.	Little or no change.	Little or no change.	Fibre becomes paler, soln. colourless or orange.	No action.	Ash contains Cr and sometimes Cu. Colour more or less bleached by boiling with bleaching powder.
H. Bismarck Brn. (180).	F. red.-brown, soln. red.	As with HCl, but darker.	F. brn.-yellow; soln. colourless.	F. unchanged, soln. brown.	F. almost decolorised.	Red or pink colour extracted.	Boiling water extracts colour; boiling glacial acetic acid still more, with yellowish-green fluorescence.
H. Phenyl Brown (199).	Colr. extracted, soln. brown-red.	...	Purple-brown colour extracted.	Reddish-brown colour extracted.	F. reduced to pink, soln. colourless.	Dark brown-red colour extracted.	
L. Benzo-Brown. Fr. Bayer & Co. (199 ?).	Dil.: F. more red-brown. Conc.: F. much darker, liq. purple-red.	F. brn.-black, liquid dark brown.	No action.	No action.	Fibre yellower and brighter, liqd. brown-yellow.	Only trace of colour extracted.	Stands light very badly.
L. Fast Brown R G. Act. Ges. Berlin (199).	F. dark red-violet, liquid violet. On dil. f. becomes brown again.	As with HCl	F. bright dark crimson red, liqd. cherry-red.	As NaOH	F. first darker, on boiling rapidly decolorised.	No action.	HNO_3: Black spot, which rapidly becomes bright red-brown.
H. Naphthylamine Brown (199).	F. brn.-yellow, soln. orange.	...	...	Fibre yellow.	F. purple, soln. pale pink.	Soln. bluish-pink.	
H. Alizarin (276).	Fibre brown-orange, colr. restored by NH_3	As with HCl	Action slight, f. bluer, liqd. tinted blue.	Fibre unchanged.	As with HCl	No action.	
H. Nitroalizarin (267).	F. paler, liqd. yellow.	F. darker, liq. orange.	F. darker, soln. colourless.	No action.	As with HCl	No action.	
L. Anthracene Brown. B. A. & S. F. (276).	F. yellower and brighter, liq. brownish-yellow.	F. brighter and redder, liq. chestnut-brn.; on diln. yellow.	F. black, liqd. grey.	F. brn.-grey, liqd. scarcely coloured.	F. brn.-yellow, liq. the same.	Only trace of colour extracted.	HNO_3: Black spot.

VI. BROWN COLOURS—*continued.*

Colouring Matter.	HCl	H_2SO_4	NaOH	NH_4OH	$SnCl_2$ and HCl	Alcohol.	Special Reactions and Remarks.
H. Peachwood Brown (334).	F. and liqd. yellowish-red.	F. yellow.-red, liq. yellow.	F. purple, liqd. cherry-red.	F. purple, liq. colourless.	F. and liquid cherry-red.		
H. Dyewood Brn.	Red or purple colour extracted.	As with HCl	Little change, liqd. tinged red.	F. unchanged, liqd. tinged red.	F. redder, solution reddish.	No action.	Ash contains Al and Fe
H. Camwood Brn. (336).	F. red, liqd. yellowish-red.	As with HCl	F. and liquid purple.	F. purple, liq. colourless.	F. and liquid cherry-red.	...	Occurs only on wool.
H. Manganese Brn. (Inorganic).	Slowly decolorised.	No action.	No action.	No action.	Rapidly decolorised.	No action.	Ash contains Mn

VII. BLACK COLOURS.

Colouring Matter.	HCl	H_2SO_4	NaOH	NH_4OH	$SnCl_2$ and HCl	Alcohol.	Special Reactions and Remarks.
H. Tannin Black (129).	Bleached to pale straw colr.; steeping afterwards in NH_3 gives red-brn. colour.	As with HCl	F. brown-grey or black.	No action.	Decolorised.	No action.	Ash contains Fe
L. Naphthol Black M. L. & Br. (200).	F. remains black, liquid reddish.	F. remains black, liquid olive-green.	Fibre remains black, liquid very slightly reddish.	No action.	On boiling f. is decolorised to bright grn.; on washing it becomes blue.	No action.	HNO_3: After some time a brown spot.
L. Brilliant Black. B. A. & S. F.	F. remains black, liquid slightly red-violet.	...	Fibre appears rather greener black, liq. violet-black.	Fibre remains black, liquid violet-black.	On boiling liq. becomes dark garnet red, finally almost decolorised; liq. colourless.	No action.	HNO_3; Dark red-brown spot.
L. Resorcin Black. D. & H.	F. yellow-grey, liquid orange-brown.	F. brown, liq. brown.	F. unchanged, liqd. slightly greenish.	No action.	F. bright brn., liquid bright brown.	No action.	HNO_3: Brown-yellow spot. The ash contains iron.

VII. BLACK COLOURS—*continued.*

Colouring Matter.	HCl.	H_2SO_4	NaOH	NH_4OH.	$SnCl_2$ and HCl	Alcohol.	Special Reactions and Remarks.
L. Wool Black. Act. Ges. Berlin (200).	F. remains black, liquid bright blue; on dil. pinky-red.	As with HCl	In the cold no action, on boiling f. dark violet; liquid violet.	No action.	F. decolorised.	No action.	HNO_3: After some moments, bright red-brown spot.
H. Aniline Black (250).	No action, or colr. becomes green-black, restored by alkalies. Acid soln. brownish.	As with HCl	No action.	No action.	F. green.-grey, colour restored by NH_3.	Boiling alcohol extracts brn.-red colour.	Bleaching powder solution changes colr. to brown-red. Several passages of fibre through concent. $KMnO_4$ and oxalic acid alternately, decolorise fibre. Weak oxidising agents have no action.
H. Alizarin Black (276).	F. orange, colr. restored with NH_3.	As with HCl	No action.	No action.	As with HCl	No action.	Ash contains Fe. Occurs only on printed calico.
L. Alizarin Black. B. A. & S. F. (276).	Fibre remains black, liquid very slight red-violet.	Fibre remains black, liquid slightly grn.-blue.	Fibre remains black, liquid slightly blue.	No action.	On boiling becomes brownish, liquid yellow.	No action.	HNO_3: After standing some minutes gives dark olive-green spot.
H. Woaded Black (313, 332).	Logwood colr. removed, indigo not affected, and fibre remains blue.	As with HCl	Logwood removed; indigo not affected.	As with NaOH	F. becomes dirty greenish-blue.	As with indigo-blue.	First remove logwood colours, &c., by boiling with dilute HCl, and test blue remaining for indigo.
H. Logwood Black (232).	F. red or olive-brown, solution deep red.	As with HCl	Solution purple.	As with NaOH	Fibre violet or greyish-red, solution red, afterwards brown.	No action.	Ash contains Fe or Cr.
L. Cachou de Laval. Poirrier.	Fibre little changed, liq. slightly grey.	F. rather yellower after washing as at first.	No action.	No action.	Fibre slightly redder or browner.	No action.	Fibres seldom dyed with cachou laval alone. As a ground colr. it is difficult to detect, unless topped with auramine, fustic, or magenta.

INDEX.

ACETOPHENONE, 23
Acid, amidobenzoic,
—— anthraflavic, 262, 263, 275
—— anthraquinone-sulphonic, 262
—— barbatoic, 316
—— Bayer's, 194
—— benzene-sulphinic, 12
—— benzoic, 1, 10
—— caffeic, 93
—— caffetannic, 93
—— carbozotic, 139
—— carminic, 363
—— catechuic, 97
—— catechu-tannic, 96, 121
—— chrysamic, 283
—— chrysophanic, 281
—— cinnamic, 30
—— coumaric, 46
—— cresotic, 2, 55
—— cresyl-sulphuric, 9
—— cumic, 1
—— cumidic, 2
—— digallic, 87
—— diorcellinic, 62, 316, 317
—— ellagic, 87, 92
—— ellagitannic, 87, 92
—— erythric, 315
—— eupitonnic, 72
—— evernic, 316
—— frangulic, 263
—— gallic, 66
—— gallotannic, 69, 86
—— hippuric, 23
—— hydrindic, 295
—— hydrocyanic, 20
—— hydrophthalic, 48
—— hydroxybenzoic, 50, 56
—— hydroxynaphthoic, 51
—— hydroxysalicylic, 61
Acid, indigosulphonic, 298
—— indigotic, 295
—— indoxylic, 294
—— iodoparaphenolsulphonic, 8
—— isatic, 296
—— isoanthraflavic, 262, 263, 275
—— isophthalic, 47
—— isopurpuric, 144
—— laccainic, 370
—— lecanoric, 62
—— lupulotannic, 96
—— mandelic, 2
—— melilotic, 46
—— metagallic, 66, 70, 88
—— mimotannic, 96
—— moric, 343
—— morintannic, 79, 344
—— nitrocinnamic, 33
—— nitrophenic, 141
—— nitrophthalic, 48
—— ornithuric, 24
—— orsellic, 62, 317
—— orsellinic, 62, 316, 317
—— ortho-nitrophenyl-propiolic, 33
—— ortho-phenolsulphonic, 4, 5
—— ortho-phthalic, 47, 48
—— ortho-sulphamidobenzoic, 26
—— ortho-sulphobenzoic, 26
—— para-rosolic, 160
—— phenolsulphonic, 1
—— phenyl-acrylic, 1, 30
—— phenyl-amido-azobenzoic, 181
—— phenyl-carbonic, 50
—— phenyl-formic, 10
—— phenyl-lactic, 2
—— phenyl-propiolic, 1, 33
—— phenyl-sulphuric, 9
—— phthalic, 47
—— picramic, 143

Acid, picric, 138, 139
———— commercial, 146
—— pipitzahoic, 284
—— protocatechuic, 61
—— purpuric, 144
—— pyrogallic, 69, 70
—— quercitannic, 79, 87, 93
—— rosolic, 161
—— ruberythic, 264
—— rufigallic, 67, 263
—— salicylic, 50
———— isomers of, 56
—— salicyluric, 61
—— Schäffer's, 194
—— sozolic, 5
—— sulphanilic, 177, 183
—— sulphindigotic, 298
—— sulphindylic, 298
—— sulphobenzoic, 26
—— sulphocarbolic, 5
—— sulphophenic, 5
—— sulphophenicic, 298
—— sulphopurpuric, 298
—— tannic, 74, 86
—— tannomelanic, 68
—— terephthalic, 47
—— toluic, 1, 2
—— tropic, 2
—— usnic, 316
—— vanillic, 62, 63
Acid-brown, 192, 199
—— -eosin, 167
—— -green, 238
—— -magenta, 217, 223, 226, 399
—— -violet, 234, 235, 406
—— -yellow, 184, 185, 187
———— D, 189
———— G, 187
———— OO, 184.
———— S, 138, 156
Acids, aromatic, 1, 2
———— appendix to, 74
—— benzoic series of, 1
—— cinnamic series of, 1
—— from lichens, 316
—— hydroxybenzoic, 56
—— naphthol-sulphonic, 194
—— nitro-phenolsulphonic, 151
—— of tan-liquors, 125
Acids, phthalic, 47
—— sulphonic, 133, 374
—— tannic, 74
Alizarin, 262, 263, 264, 274, 380, 396, 404, 407
—— blue shade, 276, 279
—— commercial, 274
—— yellow shade, 276, 279
Alizarin-black, 276, 281, 420
—— -blue, 268, 276, 379, 380
—— -brown, 271, 276, 418
—— -carmine, 267, 276
—— -green, 276
—— -orange, 267, 276
—— -paste, 274
—— -powder W., 267
—— S or sulphonated, 267, 379, 404
—— -violet, 276, 407
Alkanet, 337, 395
Alkannin, 337
Amaranth, 192, 220
Amethyst, 253, 255, 378
Amidazo-compounds, 178
———— dyes, 184
Amido-azobenzene, 179, 395
Amidonaphthols, 213
Amidophenols, 212
Amido-resorcinol, 213
Anchusin, 337
Aniline-black, 250
—— -blues, 227
—— -dyes, 132, 214
—— -greens, 237
—— -orange, 138
—— -pink, 256
—— -purple, 257
—— -red, 217, 220
—— violets, 238, 257
—— -yellow, 179
Animal tannin, 95
Anisidine-ponceau, 192
Anisol-red, 192
Annatto, 351, 417
Anthracene dyes, 261
—— -green, 276
—— -violet, 276
Anthrachrysone, 262
Anthraflavone, 263
Anthragallol, 263, 270, 276

Anthrapurpurin, 262, 263, 273, 276, 380
Anthraquinone, 261
—— hydroxy-derivatives of, 263
—— -sulphonic acids, 262
Anthrarobin, 266
Anthrarufin, 273
Archil, 320, 396, 404
—— adulterations of, 323
—— -red, 197, 224
—— -substitute, 192, 396
Aromatic acids, 1
—— balsams, 34
Aseptol, 5
Auramine, 244, 378, 395, 415
Aurantia, 138, 156, 395, 413
Aurin, 160, 379, 400
Azaleine, 220
Azarine, 209, 403
Azobenzene, 175
Azo-black, 200
Azo-blue, 204, 205, 208, 407
Azo-coccin, 192, 197
Azo-colouring matters, 175
Azo-dyes, 175, 379
—— from amido-stilbene, 204
—— from benzidine, 201, 379
—— from tolidine, 203
—— general reactions of, 210
—— sulphonated, 182
Azoeosin, 174, 403
Azoflavin, 184, 185, 190
Azolitmin, 325
Azonium bases, 254
Azophenine, 249
Azo-reds, 191
Azo-resorufin, 158
Azo-rubin, 192, 199
Azo-violet, 203, 205, 405
Azoxybenzene, 175
Azuline, 216

Balsam, copaiba, 41
—— Peruvian, 37, 40
—— tolu, 37, 40
Balsams, aromatic, 34
—— cinnamic, 37
Barwood, 335, 404
Bengaline, 250
Benzaldehyde, 18
—— -green, 241, 378
Benzidine, 201
—— dyes from, 203, 379
Benzoates, metallic, 13, 16
Benzoazurin, 203, 205, 208, 407
Benzoflavine, 289
Benzoic acid, 1, 10
—— aldehyde, 18
—— ether, 17
—— sulphinide, 26
Benzoïn, 19
—— gum, 35, 42
Benzonitril, 24
Benzopurpurin, 203, 205, 207, 396, 402
Benzoyl methide, 23
—— series, 11
—— sulphonic-imide, 26
Benzyl alcohol, 18
—— benzoate, 17
—— chloride, 12, 18
—— cinnamate, 33
—— -fluoresceïn, 166
—— -violet, 406
Betol, 60
Biebrich or imperial scarlet, 197, 212, 400
Bitter-almond oil, 19
———— water, 22
Bixin, 352
Black, alizarin-, 276, 281, 420
—— aniline-, 250, 420
—— azo-, 200
—— logwood-, 332, 420
—— naphthol-, 200, 419
—— resorcin-, 419
—— tannin-, 129, 419
—— wool-, 200, 420
Blue, alizarin-, 269, 270, 276, 397, 410
—— alkali-, 217, 227, 230, 397, 408
—— aniline-, 227
———— sulphonated, 229
—— azo-, 204, 205, 208, 397, 407
—— azo-diphenyl-, 248
—— Basle-, 252, 255, 408
—— Blackley's, 231, 250
—— Boiley's, 300
—— chemic-, 300
—— Coupier's, 250

Blue, diphenylamine-, 227, 380
—— ethylene-, 287
—— fast B and R, 249
—— fluorescent-, 159
—— Guernsey-, 250
—— indigo-, 294, 397
—— Meldola's, 253, 260, 410
—— methyl-, 232
—— methylene-, 285, 378, 397, 410
—— naphthalene-, 253, 260, 410
—— naphthol-, 253, 258
—— neutral-, 252, 255
—— new-, 253, 260, 378, 410
—— nile-, 253, 260, 410
—— phenol-, 253
—— resorcin-, 159, 397, 407
—— rosaniline-, 227, 228, 380
—— Saxony-, 300
—— soluble-, 229, 407
—— spirit-, 228, 397, 408
—— Victoria-, 232, 378, 397, 408
—— water-, 227, 231, 397
Blues, various, 227, 233, 397, 407
Bordeaux, 192
Brazileïn, 333
Brazil-wood, 333, 404
Brilliant black, 418
—— congo, 203, 205, 402
—— crocein, 198
—— green, 238, 378
—— yellow, 204, 205, 208
Bromeosin, 167, 171
Brown, acid-, 199, 200
—— anthracene-, 270, 276, 418
—— benzo-, 418
—— Bismarck-, 180, 418
—— catechu- 418
—— cinnamon-, 180
—— fast-, 192, 195, 199, 200, 418
—— leather-, 180
—— Manchester-, 180
—— naphthylamine-, 192, 418
—— phenylene-, 180, 418
—— resorcin-, 199
—— Soudan-, 182
Browns, various, 418
Butter colourings, 354

Cachou de Laval, 420
Caliatour wood, 335
Campeachy wood, 328
Cam-wood, 335
Canarin, 288, 388
Canelle, 180
Capillary analysis, 375
Cardinal, 220
Carminaphtha, 182
Carmine, 367
Carmoisin, 192, 401
Carotin, 355, 356
Carthamin, 338
Cassissine, 223
Catechin, 97, 105
Catechol, 65
—— phthaleïn, 49
Catechu, 104
Cerise, 218, 220
Chemic or Chemic blue, 300
Chlorophyll, 290
Chrome-green, 412
—— -yellow, 417
Chrysamine, 203, 205, 206, 380, 395, 414
Chrysaniline, 245
Chrysarobin, 281
Chrysazin, 273
Chryseolin, 184
Chrysoïdine, 179, 378, 395, 413
Chrysoïn, 184, 185, 188, 395
Chrysolin, 164, 166, 171
Chrysophan, 281
Chrysophenine, 204, 205, 208, 414
Cinnameïn, 33
Cinnamene, 31
Cinnamic acid, 30
—— aldehyde, 44
—— balsams, 34
—— ethers, 33
Cinnyl alcohol, 34
—— benzoate, 39
—— cinnamate, 34
Citronine, 138, 156, 190, 395, 414
Claret-red, 192, 401
Coal-tar dyes, history of, 131
———— detection of, in archil, 322
———— solubility of, 377
Coccin, 173, 192
Coccinin, 192

Cochineal, 363, 396, 405
—— ammoniacal, 367, 396, 405
—— -carmine, 367
—— -crimson and scarlet, 366
Cœrulein, 73, 379, 380, 397, 411
Cœrulignone, 73
Colouring matters, recognition of, 371
———— tables for, 377
—— absorption-spectra of, 381
—— adulterations of, 384
—— examination of, 384
—— fluorescence of, 383
—— insoluble, 380
—— nitro-, 137, 379
Congo, brilliant-, 203, 204, 205, 402
—— -corinth, 203, 204, 205, 403
—— -red, 203, 205, 206, 396, 402
—— -yellow, 203, 205
Corallin red-, 162
—— yellow-, 162
Coumarin, 46
Crocein, brilliant, 197
—— B, 197
—— -orange, 184, 414
—— -scarlet, 3 B and 7 B, 196, 400
———— 7 B extra, 192
Crocin, 349
Cudbear, 324
Curcumein, 196
Curcumin, 288, 358, 416
Cutch, 104
Cyanosin, 167, 169, 171, 380
Crystal ponceau, 192
—— violet, 233, 235, 236

Dahlia, 233
Daphnin, 169
Deltapurpurin, 203, 204, 205, 207, 402
Dextro-saccharine, 30
Diazo-amidobenzene, 177
Diazobenzene acid-sulphate, 177
—— compounds, 176
—— chloride, 176
—— nitrate, 177
—— sulphonic acid, 177
Diazo-compounds, 176
Dimethyl-amido-azobenzene, 180
———————— -sulphonic acid, 188
Dinitrocresol, 152
Dinitronaphthol, 153
Dinitrophenols, 141, 149
Diphenylamine, 213
—— -blue, 216
Divi-divi, 105
Dyes, *see* also Colouring Matters
Dyes, acid-, 133, 379
—— adjective-, 135
—— aniline-, 132
—— animal, 362
—— assaying and examining, 384
—— basic-, 132, 378
—— classification of, 136
—— coal-tar-, *see* Coal-tar Dyes.
—— compound, detection of, 362
—— from anthracene, 261
—— from lichens, 315
—— neutral, 134
—— of natural origin, 289
—— on fibres, recognition of, 389
—— on silk, recognition of, 394
———— red, 390
—— salts of basic, 373
—— substantive-, 134
—— sulphuretted, 284

Emeraldine, 251
Eosin, 167, 396, 399
—— acid-, 167
—— azo-, 174
—— ethyl-, 167
—— methyl-, 167, 399
Eosins, 167, 379
—— spirit soluble, 170, 172, 380
Erythrin, 167, 171, 315
Erythroglucin, 316, 318
Erythrol, 316, 318
Erythrosin, 167, 171, 379, 396, 400
Erythrozyme, 264
Ethyl benzoate, 17
—— -blue, 228
—— cinnamate, 33
—— -eosin, 167, 169, 171
—— orcellinate, 317
Eurhodines, 253, 257
Extraction of tannin matters, 108

Fisetin, 346
Flavaniline, 245, 378

Flavaurin, 138, 151
Flavin, 342, 416
Flavophenine, 203, 205, 206
Flavopurpurin, 262, 263, 273, 275, 380
Fluoresceïn, 49, 165
Fluoresceïns, substituted, 167
Fluorescence of colouring matters, 383
Fuchsine, 220
Fustet-wood, 345
Fustic, old, 343, 395, 417
—— young, 345, 394, 417

GALLEÏN, 73, 276, 380, 397, 405
Gallic acid, 66
Gallocyanin, 74, 253, 276, 380, 406
Galloflavin, 276, 380, 416
Gallotannic acid, 86, 120
Galls or Gall nuts, 105
Gamboge, 361
Garancine, 264
Geranium, 218
Giroflé, 253, 255
Glycocine, 25
Green, aldehyde-, 287, 397, 411
—— aniline-, 237
—— anthracene-, 276
—— basic, 238
—— brilliant-, 238, 239, 378
—— chrome-, 410
—— Helvetia-, 242, 411
—— malachite-, 241, 378, 397, 411
—— methylaniline-, 242, 378, 397, 411
—— methylene-, 378, 379
—— naphthol-, 160
—— resorcin, 158, 397, 411
—— solid, 158, 380
—— sulphonated, 238, 239, 411
Greens, various, 238–245, 397, 411
Grenadin, 218
Guaiacol, 65
Gum benjamin or benzoin, 35

HÆMATEÏN, 329
Hæmatoxylin, 328
Helianthin, 184, 185, 188, 326
—— reduction of, 211, 286
Heliochrysin, 138, 395
Heliotrope, 203, 205, 406
Hummel's tables of reactions, 398
Hydrindigotin, 296
Hydroxyanthraquinones, 263
Hydroxy-azobenzene, 182
—— compounds, 182
Hydroxychrysazin, 263
Hydroxypurpurin, 263
Hypnone, 23

INDICAN, 292
Indicators of neutrality, 326
Indigo, 290, 397
—— assay of, 302
—— -blue, *see* Indigotin
—— -brown, 293
—— -carmine, 298, 299, 397
—— commercial, 302
—— extract, 299
—— -green, 410
—— -purple, 298, 300
—— -red, 293
—— reduced, 296
—— soluble, 299
—— -substitute, 250
—— sulphonated, 299
—— -white, 296
Indigotin, 294, 397
—— -sulphonic acids, 298
—— synthesis of, 33
Indiglucin, 293
Indirubin, 293
Indole, 296
Indophenol, 253, 258, 380, 397, 408
—— reduced, 259
Indulines, 248, 380, 397, 408
—— sulphonated, 249
Ingrain colours, 210
Ink, 126
—— indelible, 128
—— marking, 129
—— -marks, 129
—— writing, 126
Iodeosin, 169, 171
Isatin, 295
—— -sulphonic acids, 296, 299

JAUNE SOLIDE, 181

KERMES, 369
Kino, 105

Kinoïn, 87, 98
Knoppern, 106

LAC-DYE, 369
Lacmoïd, 159
Laurel water, 23
Leather, 75, 118
Leucaniline, 214, 220
Leucine, 298
Lima-wood, 333
Litmus, 324
—— as an indicator, 325
Logwood, 327, 328
—— black, 332, 420
Luteolin, 190, 347

MACHROMIN, 344
Maclurin, 344
Madder, 264, 270, 327, 404, 416
Magdala red, 353, 355, 357, 380, 396, 399
Magenta, 220, 378, 396, 399
—— acid-, 223, 226, 379, 396, 399
—— commercial, 225
—— detection of, 221, 378
—— -violet, 220
Maize, 288
Mandarin, 184, 186, 188
Marigold-yellow, 354, 356
Maroon, 247, 220
Martinon's tables of reactions, 395
Mauvaniline, 247
Mauveine, 257, 378, 397
Mélinite, 143
Metacinnamene, 31
Meta-phenylenediamine, 178
Methyl-brown, 188
—— catecholate, 65
—— -eosin, 167, 171, 399
—— -orange, 188, 326
—— salicylate, 58
Methylene blue, 285, 378
—— green, 378, 379
—— red, 287
Micro-spectroscope, use of, 381
Mononitrophenols, 141, 150
Mordants, 134
Morin, 343
Muscarin, 253, 260, 378
Myrabolanes, 106

NAPHTHALENE TETRACHLORIDE, 48
—— picrate, 145
Naphthionic red, 192
Naphthol-green B, 160
—— -sulphonic acids, 194
—— -yellow, 156, 395
Naphthyl salicylate, 60
Naphthylamine-sulphonic acids, 207, 208
Nepaline, 173
Narceine, 191
Neutral blue, 252, 254
—— red, 253, 258
—— violet, 253, 258
Nigraniline, 251
Nigrosines, 248, 380
Nitro-alizarin, 267, 276, 380, 395, 396, 416, 418
Nitrobenzene, detection of, 20
Nitrobromeosin, 169, 171
Nitro-colouring matters, 137
Nitrocresols, 153
Nitronaphthols, 153
—— sulphonated, 155
Nitrophenols, 137
—— sulphonated, 137, 151
Nitroso-colouring matters, 157
—— -naphthol, 160
—— -phenol, 157
—— -resorcinol, 158

OAK-TANNIN, 93
Oil, bitter-almonds, 19
—— cassia, 45
—— cherry-birch, 59
—— cinnamon, 45
—— gaultheria, 59
—— sassafras, 59
Old fustic, 343, 395, 417
Orange, alizarin-, 267, 276
—— aniline-, 138
—— Blackley-, 138
—— crocein-, 184, 188
—— dimethyl-aniline-, *see* Helianthin
—— diphenylamine-, 189
—— ethyl-, 189
—— gold-, 188
—— I, 184, 396
—— II, 184, 185, 188, 396, 413

Orange III, 184, 188, 396, 413
—— IV, 184, 185, 190, 395, 413
—— G, 184, 188
—— MN, 184, 185, 190
—— methyl-, 184, 185, 188, 326
—— N, 184, 185, 190
—— β-naphthol-, 184
—— Palatine-, 138
—— Poirrier's-, 184
Orceïn, 319
Orchil, *see* Archil
Orcin or Orcinol, 318
Orellin, 352
Oriol, 415
Ornithine, 24
Orseille, *see* Archil
Orseillin, 197, 401
Oxazines, 253, 259

PARAROSANILINE, 214
Paste colours, 275
Peachwood, 327, 404, 419
Peonin, 182, 396
Perseo, 324
Persian berries, 348, 417
Peruvian balsam, 37, 40
Phenacetolin, 327
Phenicienne, 138
Phenol-azobenzene, 181
Phenol-phthaleïn, 164, 326
Phenol-sulphonates, 7
Phenosafranine, 250, 255
Phenyl cyanide, 24
—— -ethylene, 31
—— oxalate, 162
—— salicylate, 59
Phenyl-amido-azobenzene, 181
Phenylene-brown, 180
—— -diamine, 178
Phlobaphenes, 80, 82, 94
Phloroglucol or Phloroglucin, 85
Phloxin, 167, 171, 399
Phosphine, 245, 378, 395
Phthalanil, 49
Phthaleïns, 49, 163, 379
Phthalic acid, 47
—— anhydride, 49
Picrates of alkaloids, 144
—— of basic dyes, 144
Picrates of hydrocarbons, 145
—— of metals, 151
Picric acid, 138, 139, 394, 412
Picrocrocin, 349
Picro-erythrol, 316, 317
Piperonal, 64
Polychromine, 401
Ponceau, 184, 192, 196, 197, 400
Primrose, 167, 171, 380, 396
Primula, 233
Primulin, 191, 209, 415
—— -red, 210, 401
Protocatechuic acid, 61
Prune, 253, 259
Pseudo-erythrin, 317
Purple, French, 320
—— Hessian, 204, 205, 403
—— Perkin's-, 257, 406
—— regina-, 233, 235
—— resorcin-, 216
Purpurin, 262, 263, 270, 276, 404
Purpurogallol, 71
Purpuroxanthin, 263
Pyrocatechin, 65
Pyrogallic acid, 70
—— ethers, 72
Pyrogallol, 69, 70
Pyrosin, 167

QUERCITANNIC ACID, 79, 87, 93
Quercitin, 341
Quercitron bark, 339, 395, 416
Quinizarin, 263
Quinoline-yellow, 174, 395, 413
Quinol-phthaleïn, 49
Quinone-dioxime, 158
Quinonoxime, 157

RECOGNITION OF DYES,
—— on silk, 394
—— on fibres, 397
Red, aniline-, 217
—— anisol-, 192
—— Bengal-, 167, 396
—— claret-, 192
—— congo-, 203, 205, 206, 212
—— -corallin, 162
—— diamine-, 204, 205, 206
—— dyes on silk, 396

Red, fast, 192
—— Hessian, 204
—— imperial, *see* Biebrich scarlet
—— magdala-, *see* Magdala red
—— methylene-, 287
—— naphthalene-, 253
—— neutral, 253, 258
—— phenatol, 192
—— Soudan-, 258
—— toluylene-, 203, 208, 378
—— turkey-, 279
—— xylidine-, 191
Red dye-woods, 327, 396
Resorcin-blue, 159, 397
—— -brown, 199
—— -green, 158, 397
—— -phthaleïn, 164
—— -purple, 216
Rhodamine, 173, 400
Roccellin, 192, 396
Rosanaphthylamine, 253, 257
Rosaniline, 214, 217
—— -blue, 228, 380
—— salts, 219
Rosaurin, 161
Rosazurin, 204, 205
Rose bengale, 169, 171
—— JB, 167, 171
Roseine, 220
Rosocyanin, 360
Rosolic acid, 161
Rubeine, 217, 220
Rubeosin, 169
Rubidine, 192
Ruficarmine or Ruficoccin, 364
Rufiopin, 263
Rutin, 341

SACCHARINE, 26
Safflower, 338, 405
Saffron, 348, 356, 395
Safranine, 252, 256, 399
Safranines, 252, 255, 378
Safrosin, 167, 171, 396
Salicin, 50, 60
Salicylates, 57
Salicylic acid, 50
—— aldehyde, 60
—— ethers, 58
Salicylol, 60
Saligenol, 60
Salol, 59
Salts G and R, 194
Sandal-, Sanders-, or Santal-wood, 335, 405
Santalin, 335
—— -sulphonic acid, 335
Sapan wood, 327
Saxony blue, 300
Scarlet, Biebrich-, 197, 212, 400
—— cochineal-, 192
—— crocein-, 196, 400
—— double, 197
—— -eosin, 167, 169
—— fast, 197, 400
—— G,
—— GG, 192
—— GS, 192
—— imperial, 173, and Biebrich scarlet
—— R, 192, 195
—— 2 R, 192, 401
—— 3 R and 4 R, 197, 401
—— S, 197
—— silk, 396
—— wool-, R, 192
—— xylidine-, 191, 192
Secondary Azo-dyes, *see* Tetrazo-dyes
Soudan G, 182
—— I, 182
—— II, 182
—— III, 199
—— -brown, 182
Sozoiodol, 8
Spectra of colouring matters, 381
Spirit-blue, 227, 228
—— -green, 241
—— -violet, 233, 235
—— -yellow, 179
Stilbene, 31
Storax, 37
Styracin, 34
Styrol or Styrolene, 31
Styrone, 34
Sulphocarbolates, 7
Sulphonated azo-dyes, 182
———— aniline blues, 229
———————— greens, 238
———————— violets, 234

Sulphonated indigo, 298
—— indulines, 249, 379
—— rosaniline, 226, 379
Sulphophenates, 7
Sulphuretted dyes, 284
Sumach, 107, 395
Sun-gold, 138

TABLES for recognising dyes, 378
———— on fibres, 398
———— on silk, 394
Tan liquors, assay of, 125
Tannic acids, 74
Tanning matters, 98
—— assay of, 109
—— sampling of, 108
Tannins, assay of, 107
—— action of heat on, 78
———— alkalies on, 83
———— acids on, 81
—— constitution of, 77
—— extraction of, 76
—— phloroglucol, 84
—— recognition of, 101
—— table of principal, 79
Tannin-yielding materials, 98
Tartrazin, 288, 379, 416
Tetrabrom-fluoresceïn, 167
Tetrazo-dyes, 196
—— behaviour on reduction, 198, 212
—— reaction with sulphuric acid, 198
Thio-colouring matters, 285
Thiorubin, 288
Tolidine dyes, 202, 203
Tolu balsam, 37, 40
Toluylene orange, 414
—— red, 203, 208, 378
Tournesol, 324
Triamidophenol, 143
Trinitrophenols, 141
Triphenylcarbinol, 214
Triphenylmethane, 214
Tropæolins, 183–190
Turmeric, 357, 394, 417

URANIN, 166, 171

VALONIA, 107
Vanilla, 63
Vanillin, 62
Vanillone, 64
Vermilionette, 168
Vesuvine, 180, 378
Violaniline, 248
Violet, alizarin-, 276
—— aniline-, 233
—— anthracene-, 276
—— azo-, 203, 205, 405
—— benzyl-, 237, 406
—— crystal-, 236, 378
—— fast-, 405
—— Hessian, 204, 205, 405
—— Hofmann's, 233, 378
—— Lauth's, 285
—— methyl-, 234, 378, 397
—— neutral-, 253, 258
—— Perkin's, 257
—— solid, 74, 253, 259
—— spirit, 235, 406
Violets, various, 233–237, 405, 406
Viridin, *see* Acid-green

WEINGÄRTNER'S tables for recognising dyes, 377
Weld, 347, 395, 417
Woad, 291, 420
Wool, detection of mixed colours on, 362
Wine, detection of red colouring matters in, 211

XYLIDINE-RED, 195
—— -scarlet, 191, 195

YELLOW, acid, *see* Acid-yellow
—— aniline-, 179
—— azo-, 184, 190
—— berries, 348
—— brilliant-, 156, 184, 190, 414
—— butter-, 180
—— Chinese-, 339
—— chinoline, *see* Quinoline yellow
—— corallin-, 162
—— diphenylamine-, 184, 185, 189
—— dyes on silk, 395
—— fast-, 181, 184, 187, 413
—— gold-, 138, 152, 154
—— Hessian, 204, 414

Yellow, imperial, 138, 156
—— Indian, 190
—— Manchester-, 138, 154
—— Martius'-, 138, 154
—— metanil-, 184, 190
—— naphthalene-, 138, 154
—— naphthol-, 138, 154, 394, 413
—— naphthol- S, 138, 156
—— naphthylamine-, 138
—— N, 190
—— new, 190
Yellow, orange-, 184, 188
—— quinoline-, 174, 395, 413
—— resorcin-, 184, 186
—— solid, 181
—— spirit-, 179
—— sun-, 288
—— Victoria-, 138, 152, 412
—— -wood, 343
Yellow dye-woods, 339
Yellows, various, 395, 412
Young fustic, 345, 394, 417

ERRATA.

VOLUME I.

Page 64, column 3, sixth line of figures, *for* "89·59," *read* "89·95."

VOLUME II.

Page 15, line 20, *for* "pressure," *read* "presence."

Page 49, line 10, *for the words* "The additional thiosulphate," *substitute* "The difference between the volume of thiosulphate used in the blank experiment and that".

Page 215, combining weight of fatty acids of cotton-seed oil, *for* "337·2," *read* "287·2"; and *delete* figures for specific gravity of fatty acids from cocoanut oil and lard.

Page 246, footnote, eight lines from bottom, after the words "See also," *insert* "M. Dechan and".

Page 563, line 11 from bottom, *for* "fluorescence," *read* "fluoresceïn."

VOLUME III.

Page 8, line 15, *for* "Iodo-paraphenolsulphuric acids," *read* "Iodo-paraphenolsulphonic acids."

Page 184, first column of table, after the words "Mandarin G," *for* "(P. 188)" *read* "(P. 190)".

Page 208, line 13 from bottom of page, after the word "colour," *insert* the words "of the".

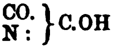
Page 209, *insert* the following footnote:—"The composition of primulin has been recently made public (A. Green, *Jour. Chem. Soc.*, lv. 227). It appears to be the sulphonic acid of a sulphuretted base, probably containing $C_{28}H_{18}N_4S_3$, obtained by heating paratoluidine with sulphur."

Page 211, line 5 from bottom, after the words "sulphuretted hydrogen," *insert* "and then adding ferric chloride till the odour of sulphuretted hydrogen has disappeared."

Page 214, in constitutional formula of rosaniline, *for* "$C_6H(CH_3).NH_2$," *read* "$C_6H_3(CH_3).NH_2$."

Page 215, last line, *for* "224," *read* "228."

Page 296, in footnote, the formula of isatin should be,



$$C_6H_4\left\{\begin{matrix}.CO.\\ .N:\end{matrix}\right\}C.OH$$

PRINTED BY NEILL AND COMPANY, EDINBURGH.

Catalogue D.]

LONDON, 11, NEW BURLINGTON STREET,

NOVEMBER, 1888.

A LIST
OF
J. & A. CHURCHILL'S
WORKS
ON
CHEMISTRY, MATERIA MEDICA,
PHARMACY, BOTANY,
THE MICROSCOPE,
AND
OTHER BRANCHES OF SCIENCE

INDEX

PAGE
Allen's Commercial Organic Analysis vi
Armatage's Veterinarian's Remembrancer xi
Baily's Physician's Pharmacopœia ... viii
Beasley's Pocket Formulary x
  Do. Druggist's Receipt Book ... x
  Do. Book of Prescriptions ... x
Bentley's Manual of Botany xii
  Do. Structural Botany xii
  Do. Systematic Botany... ... xii
Bentley and Trimen's Medicinal Plants xii
Binz's Elements of Therapeutics ... vii
Bloxam's Chemistry iii
  Do. Laboratory Teaching .. iii
Bowman's Practical Chemistry ... iv
B. P. C. Unofficial Formulary ... viii
Brown's Practical Chemistry iv
Cameron's Oils, Resins, Varnishes ... vii
  ——— Soaps and Candles ... vii
Carpenter's Microscope and its Revelations xii
Chauveau's Comparative Anatomy ... xiii
Churchill's Technological Handbooks vii
Clowes' Practical and Analytical Chemistry iv
Cook's Organic Analysis iv
Cooley's Cyclopædia of Receipts ... v
Draper's Medical Physics xiv
Dunglison's Medical Lexicon ... xv
Ekin's Potable Water xv
Ewart's Poisonous Snakes of India ... xiii
Fayrer's Poisonous Snakes of India... xiii
Flückiger's Cinchona Barks ... ..
Fownes' and Watts' Chemistry ... iii
Fox's Ozone and Antozone xv
Frankland and Japp's Inorganic Chemistry iv
Fresenius' Chemical Analysis ... iv
Gardner's Brewer, Distiller, &c. ... vii
  Do. Bleaching, Dyeing, &c. ... vii
  Do. Acetic Acid, Ammonia, &c. vii
Greene's Tables of Zoology xiv
Hardwich's Photography, by Taylor xv
Hehner's Alcohol Tables vi
Hehner and Angell's Butter Analysis vi
Hoffmann and Power's Chemical Analysis v
Huxley's Anatomy of Vertebrates ... xiv
  Do. Anatomy of Invertebrates... xiv

PAGE
James's Guide to the New B.P. ... ix
Johnson's Analysts' Companion ... iv
Kay-Shuttleworth's Modern Chemistry iv
Kohlrausch's Physical Measurements xiv
Lee's Microtomist's Vade Mecum .. xiii
Lescher's Recent Materia Medica ... viii
Marsh's Section Cutting xiii
Martin's Microscopic Mounting ... xiii
Mayne's Medical Vocabulary ... xv
Microscopical Journal (Quarterly) ... xii
Morley's Organic Chemistry v
Ord's Comparative Anatomy ... xiv
Owen's Manual of Materia Medica ... viii
Pereira's Selecta è Prescriptis ix
Pharmaceutical Journal and Transactions xi
Phillips' Materia Medica viii
Price's Photographic Manipulation ... xv
Proctor's Practical Pharmacy ... ix
Rodwell's Natural Philosophy ... xiv
Royle's Materia Medica vii
Shea's Animal Physiology xiii
Smith's Pharmaceutical Guide ... x
Southall's Materia Medica viii
Squire's Companion to the Pharmacopœia ix
Squire's Hospital Pharmacopœias ... ix
Steggall's First Lines for Chemists ... x
Stillé and Maisch's National Dispensatory vii
Stowe's Toxicological Chart x
Sutton's Volumetric Analysis ... vi
Taylor on Poisons x
Thorowgood's Materia Medica .. vii
Tirard's Prescriber's Pharmacopœia... ix
Tuson's Veterinary Pharmacopœia ... xi
Vacher's Primer of Chemistry . iii
Valentin's Qualitative Analysis ... v
  Do. Chemical Tables v
Wagner's Chemical Technology ... vi
Wahltuch's Dictionary of Materia Medica viii
Watts' Inorganic Chemistry iii
  Do. Organic Chemistry iii
Williams' Veterinary Medicine ... xi
  Do. Veterinary Surgery ... xi
Wilson's Zoology xiv
Wittstein's Pharmaceutical Chemistry xi
Year Book of Pharmacy xi

⁂ The Works advertised in this Catalogue may be obtained through any Bookseller in the United Kingdom, or direct from the Publishers, on Remittance of their cost.

A LIST OF

J. & A. CHURCHILL'S WORKS

ON SCIENCE

C. L. Bloxam

CHEMISTRY, INORGANIC and ORGANIC. With Experiments. By CHARLES L. BLOXAM, late Professor of Chemistry in King's College, London, and in the Department for Artillery Studies, Woolwich. Sixth Edition. With 335 Engravings . 8vo, 18s.

By the same Author

LABORATORY TEACHING: Or, Progressive Exercises in Practical Chemistry. Fifth Edition. With 89 Engravings. Crown 8vo, 5s. 6d.

H. Watts

PHYSICAL AND INORGANIC CHEMISTRY. By HENRY WATTS, B.A., F.R.S., late Editor of the *Journal of the Chemical Society;* Author of "A Dictionary of Chemistry," &c. With Coloured Plate of Spectra, and 150 Wood Engravings . . Crown 8vo, 9s.

H. Watts and W. A. Tilden

CHEMISTRY OF CARBON COMPOUNDS; or, ORGANIC CHEMISTRY. By HENRY WATTS, B.A., F.R.S. Second Edition, by WILLIAM A. TILDEN, D.Sc., F.R.S., Professor of Chemistry in the Mason College, Birmingham. With Engravings . Crown 8vo, 10s.

⁂ These two volumes are based on the well-known Manual of the late Professor Fownes, and form the Thirteenth Edition of that work.

F. Clowes

PRACTICAL CHEMISTRY AND QUALITATIVE INORGANIC ANALYSIS. By FRANK CLOWES, D.Sc. Lond., F.C.S. Lond. and Berlin, Professor of Chemistry at the University College, Nottingham. Fourth Edition, with 55 Engravings and Frontispiece. Post 8vo, 7s. 6d.

⁂ Adapted for use in the Laboratories of Schools and Colleges.

A. Vacher

A PRIMER OF CHEMISTRY, Including Analysis By ARTHUR VACHER . . . . 18mo, 1s.

R. Fresenius

QUALITATIVE ANALYSIS. Translated by CHARLES E. GROVES, F.R.S. Tenth Edition, with Coloured Plate of Spectra and 46 Engravings . . . . . . 8vo, 15s.

By the same Author

QUANTITATIVE ANALYSIS. Seventh Edition.
Vol. 1. Translated by A. VACHER. With 106 Engravings . 8vo, 15s.
Vol. 2. Parts 1 and 2. Translated by C. E. GROVES, F.R.S. With Engravings. 8vo, 2s. 6d. each.

J. E. Bowman and C. L. Bloxam

PRACTICAL CHEMISTRY, Including Analysis. By JOHN E. BOWMAN and CHARLES L. BLOXAM. Eighth Edition. With 90 Engravings . . . . Fcap 8vo, 5s. 6d.

⁂ In this edition the portion devoted to Quantitative Analysis has been considerably enlarged, and a separate chapter has been devoted to Volumetric Analysis. The nomenclature has also been brought up to date.

E. Frankland and F. R. Japp

INORGANIC CHEMISTRY. By EDWARD FRANKLAND, Ph.D., D.C.L., LL.D., F.R.S., Professor of Chemistry in the Normal School of Science, and FRANCIS R. JAPP, M.A., Ph.D., F.I.C., Assistant Professor in the School. With numerous Illustrations on Stone and Wood . 8vo, 24s.

U. J. Kay-Shuttleworth

FIRST PRINCIPLES OF MODERN CHEMISTRY. By Sir U. J. KAY-SHUTTLEWORTH, Bart. Second Edition. Crown 8vo, 4s. 6d.

J. Campbell Brown

PRACTICAL CHEMISTRY. PART I. Qualitative Exercises and Analytical Tables for Students. By J. CAMPBELL BROWN, D.Sc.(Lond.), Professor of Chemistry in Victoria University and University College, Liverpool. Third Edition . . . . 8vo, 2s. 6d.

A. E. Johnson

THE ANALYST'S LABORATORY COMPANION. By ALFRED E. JOHNSON, Assoc. R.C.Sc.I., F.I.C., F.C.S., First Prizeman in Chemistry, Physics, and Mathematics, R.C.Sc.I. . Crown 8vo, 5s.

E. H. Cook

INTRODUCTORY INORGANIC ANALYSIS. A First Course of Chemical Testing. By ERNEST H. COOK, D.Sc.Lond., F.C.S., Assoc. Roy. Coll. Sci.; Physical Science Master, Merchant Venturers' School, Bristol. . . . . Crown 8vo, 1s. 6d.

H. Forster Morley

OUTLINES OF ORGANIC CHEMISTRY. By H. FORSTER MORLEY, M. A., D.Sc., Joint Editor of Watts' "Dictionary of Chemistry." Crown 8vo, 7s. 6d.

* * *

W. G. Valentin, W. R. Hodgkinson, H. Chapman-Jones, and F. E. Matthews

VALENTIN'S QUALITATIVE CHEMICAL ANALYSIS. Seventh Edition. By Dr. W. R. HODGKINSON, F.R.S.E., Professor of Chemistry and Physics, Royal Military Academy, and Artillery College, Woolwich; assisted by H. CHAPMAN-JONES, F.C.S., Demonstrator in the Royal School of Mines, &c., and F. E. MATTHEWS, Ph.D., of Cooper's Hill College. With Engravings and Map of Spectra . 8vo, 8s. 6d.

By the same Authors

TABLES FOR THE QUALITATIVE ANALYSIS OF SIMPLE AND COMPOUND SUBSTANCES, both in the Dry and Wet Way. With Map of Spectra . . . 8vo, 2s. 6d.

* * *

W. G. Valentin

CHEMICAL TABLES FOR THE LECTURE ROOM AND LABORATORY. Bv WM. G. VALENTIN, F.C.S., late Principal Demonstrator of Practical Chemistry in the Royal School of Mines and Science Training Schools, South Kensington. In five large sheets . 5s. 6d.

* * *

F. Hoffmann and F. B. Power

A MANUAL OF CHEMICAL ANALYSIS, AS APPLIED TO THE EXAMINATION OF MEDICINAL CHEMICALS. For the use of Pharmacists, Physicians, Druggists, Manufacturing Chemists, and Pharmaceutical aad Medical Students. By FREDERICK HOFFMANN, A.M., Ph.D.. Public Analyst to the State of New York, &c.; and FREDERICK B. POWER, Ph.D., Professor of Analytical Chemistry in the Philadelphia College of Pharmacy. Third Edition, with 179 Engravings. 8vo, 18s.

* * *

F. A. Flückiger

THE CINCHONA BARKS: Pharmacognostically Considered. By FRIEDRICH A. FLÜCKIGER, Ph.D., Professor in the University of Strasburg, Germany. Translated from the Original Text, with some additional Notes, by FREDERICK B. POWER, Ph.D., Professor of Pharmacy and Materia Medica in the University of Wisconsin. With 8 Lithographic Plates and 1 Woodcut . . . . Royal 8vo, 7s

* * *

R. V. Tuson

COOLEY'S CYCLOPÆDIA OF PRACTICAL RECEIPTS, AND COLLATERAL INFORMATION IN THE ARTS, MANUFACTURES, PROFESSIONS, AND TRADES: Including Medicine, Pharmacy, Hygiene and Domestic Economy. Designed as a Comprehensive Supplement to the Pharmacopœias and General Book of Reference for the Manufacturer, Tradesman, Amateur, and Heads of Families. Sixth Edition, Revised and Rewritten by Professor RICHARD V. TUSON, F.I.C., F.C.S., assisted by several Scientific Contributors. With many Engravings. 2 Vols., 1,800 pp. . . 8vo, 42s.

A. H. Allen

COMMERCIAL ORGANIC ANALYSIS; A Treatise on the Properties, Modes of Assaying, Proximate Analytical Examination, &c., of the various Organic Chemicals and Products employed in the Arts, Manufactures, Medicine, &c. With Concise Methods for the Detection and Determination of their Impurities, Adulterations, and Products of Decomposition. In 3 Volumes. By ALFRED H. ALLEN, F.I.C., F.C.S., Public Analyst for the West Riding of Yorkshire, the Northern Division of Derbyshire, &c. Second Edition.

Vol. I.—Alcohols, Neutral Alcoholic Derivatives, Sugars, Starch and its Isomers, Vegetable Acids, &c. With Illustrations 8vo. 14s.

Vol. II.—Fixed Oils and Fats, Hydrocarbons, Phenols, &c. With Illustrations . . . . 8vo, 17s. 6d.

Vol. III.—Aromatic Acids, Tannins, Colouring Matters, Cyanogen Compounds, Organic Bases, Albuminoids, &c. 8vo. [*In the Press.*]

F. Sutton

A SYSTEMATIC HANDBOOK OF VOLUMETRIC ANALYSIS; or, the Quantitative Estimation of Chemical Substances by Measure, applied to Liquids, Solids, and Gases. Adapted to the requirements of Pure Chemical Research, Pathological Chemistry, Pharmacy, Metallurgy, Manufacturing Chemistry, Photography, &c., and for the Valuation of Substances used in Commerce, Agriculture, and the Arts. By FRANCIS SUTTON, F.C.S., F.I.C., Public Analyst for the County of Norfolk. Fifth Edition, with 90 Engravings . . 8vo, 16s.

O. Hehner

ALCOHOL TABLES, giving for all Specific Gravities, from 1·0000 to 0·7938 the Percentages of Absolute Alcohol, by Weight and by Volume, and of Proof Spirit. By OTTO HEHNER, F.C.S., Public Analyst for the Isle of Wight and for the Boroughs of Derby and Ryde. Roy. 8vo, 3s. 6d.

O. Hehner and A. Angell

BUTTER; Its Analysis and Adulterations, specially treating on the Detection and Determination of Foreign Fats. By OTTO HEHNER, F.C.S., and ARTHUR ANGELL, F.R.M.S., Public Analyst for the County of Southampton. Second Edition. Entirely re-written and augmented. Crown 8vo, 3s. 6d.

R. Wagner and W. Crookes

HANDBOOK OF CHEMICAL TECHNOLOGY. By RUDOLF WAGNER, Ph.D., Professor of Chemical Technology at the University of Wurtzburg. Translated and Edited from the Eighth German Edition, with Extensive Additions, by WILLIAM CROOKES, F.R.S. With 336 Engravings . . . . 8vo, 25s.

⁂ The design of this work is to show the application of the science of chemistry to the various manufactures and industries. The subjects are treated of in eight divisions, as follows:—1. Chemical Metallurgy, Alloys, and Preparations made and obtained from Metals. 2. Crude Materials and Products of Chemical Industry. 3. Glass, Ceramic Ware, Gypsum, Lime, Mortar. 4. Vegetable Fibres. 5. Animal Substances. 6. Dyeing and Calico Printing. 7. Artificial Light. 8. Fuel and Heating Apparatus.

CHURCHILL'S TECHNOLOGICAL HANDBOOKS.

Edited by John Gardner, F.I.C., F.C.S., and James Cameron, F.I.C.,
Analyst in the Laboratory of Somerset House.

THE BREWER, DISTILLER, AND WINE MANUFACTURER: Giving directions for the Manufacture of Beers, Spirits, Wines, Liqueurs, &c. With Engravings . . Crown 8vo, 6s. 6d.

BLEACHING, DYEING, AND CALICO PRINTING. With Formulæ. With Engravings . . . Crown 8vo, 5s.

ACETIC ACID AND VINEGAR, AMMONIA, AND ALUM. With 28 Engravings . . . . Crown 8vo, 5s.

OILS, RESINS, AND VARNISHES. With Engravings. Crown 8vo, 7s. 6d.

SOAPS AND CANDLES. With 54 Engravings. Crown 8vo, 7s.

J. F. Royle and J. Harley

ROYLE'S MANUAL OF MATERIA MEDICA AND THERAPEUTICS. Sixth Edition. With Supplement of Additions and Alterations contained in the B.P. 1885. By JOHN HARLEY, M.D., F.R.C.P. With 139 Engravings . . . Crown 8vo, 15s.

"This Manual is, to our minds, unrivalled in any language for condensation, accuracy, and completeness of information. — *British Medical Journal.*

Stillé and Maisch

THE NATIONAL DISPENSATORY; containing the Natural History, Chemistry, Pharmacy, Actions and Uses of Medicines, including those recognised in the Pharmacopœias of the United States, Great Britain and Germany, with numerous references to the French Codex. By ALFRED STILLÉ, M.D., LL.D., Professor of Medicine in the University of Pennsylvania; and JOHN M. MAISCH, Phar.D., Professor of Materia Medica and Botany in the Philadelphia College of Pharmacy. Fourth Edition, with 311 Engravings. 1,781 pp. . . . . . 8vo, 36s.

C. Binz

THE ELEMENTS OF THERAPEUTICS. A Clinical Guide to the Action of Drugs. By C. BINZ, M.D., Professor of Pharmacology in the University of Bonn. Translated and Edited with Additions, in Conformity with the British and American Pharmacopœias, by EDWARD I. SPARKS, F.R.C.P., M.A., M.B. Oxon., formerly Radcliffe Travelling Fellow . . . . . Crown 8vo, 8s. 6d.

J. C. Thorowgood

THE STUDENT'S GUIDE TO MATERIA MEDICA AND THERAPEUTICS, in accordance with the British Pharmacopœia. By JOHN C. THOROWGOOD, M.D. Lond., F.R.C.P., Lecturer on Materia Medica at the Middlesex Hospital. Second Edition, with Engravings Fcap. 8vo, 7s.

C. D. F. Phillips

MATERIA MEDICA AND THERAPEUTICS: By CHARLES D. F. PHILLIPS, M.D., F.R.S. Edin. Vegetable Kingdom—Organic Compounds—Animal Kingdom . . . . 8vo, 25s.

—o—

I. Owen

MATERIA MEDICA; a Manual for the Use of Students. By ISAMBARD OWEN, M.D., F.R.C.P., Lecturer on Materia Medica and Therapeutics at St. George's Hospital. Second Edition Crown 8vo, 6s. 6d.

—o—

W. Southall

THE ORGANIC MATERIA MEDICA OF THE BRITISH PHARMACOPŒIA, systematically arranged; with Brief Notices of the Remedies contained in the Indian and U.S. Pharmacopœias, and Short Descriptions of their Chief Adulterants and Substitutions. By W. SOUTHALL, F.L.S. Fourth Edition . . . . Crown 8vo, 5s.

—o—

F. H. Lescher

RECENT MATERIA MEDICA. Notes on their Origin and Therapeutics. By F. HARWOOD LESCHER, F.C.S., Pereira Medallist. Third Edition . . . . 8vo, 2s. 6d.

—o—

A. Wahltuch

A DICTIONARY OF MATERIA MEDICA AND THERAPEUTICS. By ADOLPHE WAHLTUCH, M.D. . . 8vo, 10s. 6d.

⁂ The purpose of this work is to give a tabular arrangement of all drugs specified in the British Pharmacopœia of 1867. Every table is divided into six parts:—(1) *The Name and Synonyms*; (2) *Character and Properties or Composition*; (3) *Physiological Effects and Therapeutics*; (4) *Form and Doses*; (5) *Preparations*; (6) *Prescriptions*. Other matter elucidatory of the Pharmacopœia is added to the work.

—o—

J. Baily

A PHYSICIAN'S PHARMACOPŒIA. (Contraction Ph. Ph.) Containing Prescriptions for the Novel Method of Preparing Lozenges, including Nitro-Glycerine, Cocaine, &c., and other active remedies in exact doses. By J. BAILY, Pharmacist, Margate.
Royal 24mo, leather binding, 3s. 6d.

—o—

British Pharmaceutical Conference

THE B. P. C. Unofficial Formulary, 1888. Compiled by a Committee of the British Pharmaceutical Conference.
8vo, 6d.; or Interleaved, cloth, 1s.

N. Tirard

THE PRESCRIBER'S PHARMACOPŒIA: containing all the Medicines in the British Pharmacopœia arranged in Classes according to their Action, with their Composition and Doses. Sixth Edition. By Nestor Tirard, M.D., M.R.C.P., Professor of Materia Medica and Therapeutics in King's College, London Fcap. 32mo, bound in leather, 3s.

B. S. Proctor

LECTURES ON PRACTICAL PHARMACY. By Barnard S. Proctor, formerly Lecturer on Pharmacy at the College of Medicine, Newcastle-on-Tyne. Second Edition. With 44 Wood Engravings and 32 Lithograph Fac-Simile Prescriptions .. 8vo, 14s.

J. Pereira

SELECTA È PRESCRIPTIS. Selections from Physicians' Prescriptions. Containing Lists of Terms, Phrases, Contractions, Abbreviations, Grammatical Construction, Rules for Pronunciation, Vocabulary, &c. With a Series of Abbreviated Prescriptions and Key to the same, with Translations. For the Use of Students. By Jonathan Pereira, M.D., F.R.S. Seventeenth Edition . . . . 24mo, 5s.

P. Squire

COMPANION TO THE BRITISH PHARMACOPŒIA (latest Edition), comparing the strength of its various preparations with those of the United States, and other Foreign Pharmacopœias, to which are added Non-official Preparations, and Practical Hints on Prescribing; also a Tabular Arrangement of Materia Medica for Students, an Appendix containing Articles employed in Chemical Testing, and Analyses of the Principal Spas of Europe. By Peter Squire, F.L.S. Edited by his Sons P. W. Squire, F.L.S., F.C.S., and A. H. Squire. Fourteenth Edition. 8vo, 10s. 6d.

By the same Author

PHARMACOPŒIAS OF THE LONDON HOSPITALS. Fifth Edition . . . . Fcap 8vo, 6s.

⁂ Mr. Squire has collected all the Formulæ used in twenty-five of the principal Hospitals of London, and arranged them in groups for comparison. These Formulæ were revised and approved by the medical staff of each of the Hospitals, and may therefore be taken as an excellent guide to the medical practitioner, both as to dose and best menstruum in prescribing. The Diet Tables of the Hospitals are also included.

Prosser James.

GUIDE TO THE NEW B.P. Epitome of Changes, and Account of all the New Preparations. Their Characters, Actions, Uses, &c. With Full Therapeutical Commentary. By Prosser James, M.D., Lecturer on Materia Medica and Therapeutics at the London Hospital. Second Edition . . . . . . Crown 8vo, 2s. 6d.

J. Steggall

FIRST LINES FOR CHEMISTS AND DRUGGISTS preparing for Examination at the Pharmaceutical Society. By JOHN STEGGALL, M.D. Third Edition . . . . . . 18mo, 3s. 6d.

—o—

J. B. Smith

PHARMACEUTICAL GUIDE TO THE FIRST AND SECOND EXAMINATIONS. By JOHN BARKER SMITH. Second Edition . . . . Crown 8vo, 6s. 6d.

LATIN GRAMMAR—FRACTIONS — METRIC SYSTEM — MATERIA MEDICA — BOTANY —PHARMACY—CHEMISTRY—PRESCRIPTIONS.

—o—

A. S. Taylor

POISONS IN RELATION TO MEDICAL JURISPRUDENCE AND MEDICINE. By ALFRED S. TAYLOR, M.D., F.R.S., late Professor of Medical Jurisprudence to Guy's Hospital. Third Edition, with 104 Engravings . . . . Crown 8vo, 16s.

—o—

W. Stowe

A TOXICOLOGICAL CHART, Exhibiting at one view the Symptoms, Treatment, and Mode of Detecting the Various Poisons, Mineral, Vegetable, and Animal. To which are added concise Directions for the Treatment of Suspended Animation. By WILLIAM STOWE, M.R.C.S.E. Thirteenth Edition. . . . . Sheet, 2s.; Roller, 5s.

—o—

H. Beasley

THE POCKET FORMULARY AND SYNOPSIS OF THE BRITISH AND FOREIGN PHARMACOPŒIAS: containing all the Formulæ of the B.P. of 1885, and comprising Standard, approved, and most recent Formulæ for the Preparations and Compounds employed in Medical Practice. By HENRY BEASLEY. Eleventh Edition. 18mo, 6s. 6d.

By the same Author

THE DRUGGIST'S GENERAL RECEIPT-BOOK: Comprising a Copious Veterinary Formulary; Numerous Recipes in Patent and Proprietary Medicines, Druggists' Nostrums, &c.; Perfumery, and Cosmetics; Beverages, Dietetic Articles and Condiments; Photographic Chemicals and Formulæ; Trade Chemicals; Scientific Processes; and an Appendix of Useful Tables. Ninth Edition . 18mo, 6s. 6d.

Also

THE BOOK OF PRESCRIPTIONS: Containing upwards of 3,000 Prescriptions collected from the Practice of the most eminent Physicians and Surgeons. English and Foreign. Comprising also a Compendious History of the Materia Medica, Lists of the Doses of all Official or Established Preparations, and an Index of Diseases and Remedies. Sixth Edition . . . . 18mo, 6s. 6d.

"Mr. Beasley's 'Pocket Formulary,' Druggist's Receipt-Book,' and 'Book of Prescriptions' form a compact library of reference admirably suited for the dispensing desk."—*Chemist and Druggist.*

THE PHARMACEUTICAL JOURNAL AND TRANSACTIONS.

Published weekly. Price 4d. Annual subscription, post free, 20s.

THE YEAR-BOOK OF PHARMACY: Containing the Proceedings at the Yearly Meeting of the British Pharmaceutical Conference, and a Report on the Progress of Pharmacy,

which includes notices of all Pharmaceutical Papers, new Processes, Preparations, and Formulæ published throughout the world. Published annually in December.

8vo, 1873 to 1887—10s. each yearly volume.

General Index to the Volumes for 1864 to 1885 inclusive . . 3s. 6d.

G. C. Wittstein

PRACTICAL PHARMACEUTICAL CHEMISTRY: An Explanation of Chemical and Pharmaceutical Processes;

with the Methods of Testing the Purity of the Preparations, deduced from Original Experiments. By Dr. G. C. WITTSTEIN. Translated from the Second German Edition by STEPHEN DARBY . . . . 18mo, 6s.

"It would be impossible too strongly to recommend this work to the beginner, for the completeness of its explanations, by following which he will become well grounded in practical chemistry."—*From the Introduction by Dr. Buchner.*

R. V. Tuson

A PHARMACOPŒIA, INCLUDING THE OUTLINES OF MATERIA MEDICA AND THERAPEUTICS, for the Use of Practitioners and Students of Veterinary Medicine.

By RICHARD V. TUSON, F.I.C., late Professor of Chemistry, Materia Medica and Toxicology at the Royal Veterinary College. Fourth Edition . . Post 8vo, 7s. 6d.

"Not only practitioners and students of veterinary medicine, but chemists and druggists will find that this book supplies a want in veterinary literature."—*Chemist and Druggist.*

G. Armatage

THE VETERINARIAN'S POCKET REMEMBRANCER:

being Concise Directions for the Treatment of Urgent or Rare Cases, embracing Semeiology, Diagnosis, Prognosis, Surgery, Therapeutics, Toxicology, Detection of Poisons by their Appropriate Tests, Hygiene, &c. By GEORGE ARMATAGE, M.R.C.V.S. Second Edition . Post 8vo, 3s.

W. Williams

THE PRINCIPLES AND PRACTICE OF VETERINARY MEDICINE.

By WILLIAM WILLIAMS, F.R.C.V.S., F.R.S.E., Principal, and Professor of Veterinary Medicine and Surgery at the New Veterinary College, Edinburgh. Fifth Edition, with several Coloured Plates and Woodcuts . . . . 8vo. 30s.

By the same Author

THE PRINCIPLES AND PRACTICE OF VETERINARY SURGERY.

Fifth Edition. With Plates and 139 Woodcuts.

8vo, 30s.

R. Bentley and H. Trimen

MEDICINAL PLANTS: being Descriptions with Original Figures of the Principal Plants employed in Medicine, and an Account of their Properties and Uses. By ROBERT BENTLEY, F.L.S., late Professor of Botany in King's College, and to the Pharmaceutical Society; and HENRY TRIMEN, M.B., F.R.S., F.L.S., late Lecturer on Botany in St. Mary's Hospital Medical School. In 4 Vols., large 8vo, with 306 Coloured Plates, bound in half morocco, gilt edges, £11 11s.

——*o*——

R. Bentley

A MANUAL OF BOTANY: Including the Structure, Classification, Properties, Uses and Functions of Plants. By ROBERT BENTLEY, F.L.S., late Professor of Botany in King's College, and to the Pharmaceutical Society. Fifth Edition, with 1,178 Engravings Crown 8vo, 15s.

"As the standard manual of botany its position is undisputed."—*Chemist and Druggist.*

By the same Author

THE STUDENT'S GUIDE TO STRUCTURAL, MORPHOLOGICAL, AND PHYSIOLOGICAL BOTANY. With 660 Engravings . . . . Fcap. 8vo, 7s. 6d

Also

THE STUDENT'S GUIDE TO SYSTEMATIC BOTANY, including the Classification of Plants and Descriptive Botany. With 357 Engravings . . . . Fcap. 8vo, 3s. 6d.

——*o*——

W. B. Carpenter

THE MICROSCOPE AND ITS REVELATIONS. By W. B. CARPENTER, C.B., M.D., F.R.S. Sixth Edition, with 26 Plates, 502 Wood Engravings, and a Coloured Frontispiece . Crown 8vo, 16s.

⁂ The author has aimed to combine within a moderate compass that information in regard to the use of his instrument and its appliances, which is most essential to the working microscopist, with such an account of the objects best fitted for his study as may qualify him to comprehend what he observes, and thus prepare him to benefit science, whilst expanding and refreshing his own mind.

——*o*——

THE QUARTERLY JOURNAL OF MICROSCOPICAL SCIENCE. (Established in 1852.) Edited by E. RAY LANKESTER, M.A., LL.D., F.R.S., Professor of Zoology in University College, London; with the co-operation of E. KLEIN, M.D., F.R.S., H. N. MOSELEY, M.A., LL.D., F.R.S., and ADAM SEDGWICK, M.A., F.R.S. . Each Number, 10s.

⁂ Most of the Memoirs are illustrated by Woodcuts and Lithographic Plates, many being Coloured. The Journal contains, in addition, Notes and Memoranda, Reviews of Books, Quarterly Chronicle, and Proceedings of Societies.

S. Marsh

SECTION CUTTING: a Practical Guide to the Preparation and Mounting of Sections for the Microscope, special prominence being given to the subject of Animal Sections. By Dr. SYLVESTER MARSH. Second Edition, with 17 Engravings . . . . Fcap. 8vo, 3s. 6d.

* * *

J. H. Martin

A MANUAL OF MICROSCOPIC MOUNTING; with Notes on the Collection and Examination of Objects. By JOHN H. MARTIN, Member of the Society of Public Analysts, author of "Microscopic Objects." Second Edition. With 150 Engravings . . . . . 8vo, 7s. 6d.

* * *

A. B. Lee

THE MICROTOMIST'S VADE-MEÇUM: a Handbook of the Methods of Microscopic Anatomy, comprising upwards of 600 Formulæ and Methods collected from the practice of the best workers. By ARTHUR BOLLES LEE . : . . Crown 8vo, 8s. 6d.

* * *

J. Fayrer

THE THANATOPHIDIA OF INDIA; being a Description of the Venomous Snakes of the Indian Peninsula. With an Account of the Influence of their Poison on Life, and a Series of Experiments. By Sir J. FAYRER, K.C.S.I., LL.D., M.D., F.R.S., Physician to the Secretary of State for India in Council; late President of the Asiatic Society of Bengal. Second Edition, with 31 Plates (28 Coloured) . Folio, 7*l.* 7s.

* * *

J. Ewart

THE POISONOUS SNAKES OF INDIA. Compiled by JOSEPH EWART, M.D., F.R.C.P., Surgeon-Major in the Bengal Army, President of the Snake Poison Commission. With 21 Plates (19 being Coloured) . . . . Crown 4to, 31s. 6d.

* * *

A. Chauveau and G. Fleming

CHAUVEAU'S COMPARATIVE ANATOMY OF THE DOMESTICATED ANIMALS. Translated from the Second French Edition, and Edited by GEORGE FLEMING, F.R.G.S., Principal Veterinary Surgeon of the Army; Author of "Travels on Horseback in Mantchu Tartary," "Horse-shoes and Horse-shoeing," "Animal Plagues," etc. With 450 Engravings . . . . . . 8vo, 31s. 6d.

"We have nothing but praise to bestow on the manner in which Mr. Fleming has performed his work."—*Medico-Chirurgical Review.*

* * *

J. Shea

A MANUAL OF ANIMAL PHYSIOLOGY. With Appendix of Examination Questions. By JOHN SHEA, M.D., B.A. Lond. With numerous Engravings . . . . Fcap 8vo, 5s. 6d.

T. H. Huxley

A MANUAL OF THE ANATOMY OF INVERTEBRATED ANIMALS. By Prof. Huxley, LL.D., F.R.S. With 158 Engravings. Post 8vo, 16s.

By the same Author

A MANUAL OF THE ANATOMY OF VERTEBRATED ANIMALS. With 110 Engravings . . . . Post 8vo, 12s.

W. M. Ord

NOTES ON COMPARATIVE ANATOMY: a Syllabus of a Course of Lectures delivered at St. Thomas's Hospital. By William Miller Ord, M.B. Lond., M.R.C.P., Physician to the Hospital, and Lecturer in its Medical School . . . . Crown 8vo, 5s.

J. R. Greene

TABLES OF ZOOLOGY: indicating the Tribes, Sub-Orders, Orders, and Higher Groups of the Animal Kingdom, for Students, Lecturers, and others. By J. Reay Greene, M.D., late Professor of Natural History in the Queen's University in Ireland. Three large sheets, 5s. the set; or, mounted on canvas, with roller and varnished . . 12s. 6d.

A. Wilson

THE STUDENT'S GUIDE TO ZOOLOGY: A Manual of the Principles of Zoological Science. By Andrew Wilson, Author of "Elements of Zoology," and Lecturer on Zoology, Edinburgh. With Engravings . . . . Fcap 8vo, 6s. 6d.

F. Kohlrausch

AN INTRODUCTION TO PHYSICAL MEASUREMENTS. With Appendices on Absolute Electrical Measurement, etc. By Dr. F. Kohlrausch, Professor in Ordinary at the University of Würzburg. Second Edition. Translated from the Fourth German Edition by T. H. Waller, B.A., B.Sc., and H. R. Procter, F.C.S. With 37 Engravings. 8vo, 15s.

J. C. Draper

A TEXT-BOOK OF MEDICAL PHYSICS, for the Use of Students and Practitioners of Medicine. By John C. Draper, M.D., LL.D., Professor of Chemistry and Physics in the Medical Department of the University of New York. With 377 Engravings . 8vo, 18s.

G. F. Rodwell

NOTES ON NATURAL PHILOSOPHY, Lectures delivered at Guy's Hospital, by G. F. Rodwell, F.R.A.S., Science Master in Marlborough College. With 48 Engravings. Fcap 8vo 5s.

L. Price

A MANUAL OF PHOTOGRAPHIC MANIPULATION.

By LAKE PRICE. Second Edition, with numerous Engravings.
Crown 8vo, 6s. 6d.

⁂ Amongst the Contents are the Practical Treatment of Portraits—Groups in the Studio—Landscapes—Groups in Open Air—Instantaneous Pictures—Animals—Architecture—Marine Subjects—Still Life—Copying of Pictures, Prints, Drawings, Manuscripts, Interiors—Stereoscopy in Microphotography, &c., and Notices of the last Inventions and Improvements in Lenses, Apparatus, &c.

—o—

T. F. Hardwich and J. Traill Taylor

HARDWICH'S MANUAL OF PHOTOGRAPHIC CHEMISTRY, Theoretical and Practical. Ninth Edition. By J. TRAILL TAYLOR, Editor of the *Photographic Times and American Photographer*, and formerly Editor of the *British Journal of Photography*. With 57 Engravings . . . . Fcap. 8vo. 7s. 6d.

—o—

C. B. Fox

OZONE AND ANTOZONE: their History and Nature. By CORNELIUS B. FOX, M.D., late Medical Officer of Health for Central and East Essex. With Coloured Plates . . 8vo, 12s. 6d.

—o—

C. Ekin

POTABLE WATER: How to form a Judgment on the Suitableness of Water for Drinking Purposes. Addressed to Medical Officers of Health, and Sanitary Authorities, &c. Second Edition. By CHARLES EKIN, F.C.S. . . Crown 8vo, 2s.

—o—

R. Dunglison

MEDICAL LEXICON: A DICTIONARY OF MEDICAL SCIENCE. Containing a Concise Explanation of the various Subjects and Terms of Anatomy, Physiology, Pathology, Hygiene, Therapeutics, Pharmacology, Pharmacy, Surgery, Obstetrics, Medical Jurisprudence, and Dentistry, Notices of Climate and of Mineral Waters, Formulæ for Officinal, Empirical, and Dietetic Preparations; with the Accentuation and Etymology of the Terms, and the French and other Synonyms. By ROBLEY DUNGLISON, M.D. New Edition, by RICHARD J. DUNGLISON, M.D.
Royal 8vo (1,130 pp.), 28s.

"This title, ambitious and exhaustible as it is, simply and truthfully describes this most valuable and learned work, which briefly but distinctly gives any one who consults it, in the most accessible form, a vast amount of information on medical terminology of all kinds."—*Edinburgh Medical Journal.*

—o—

R. G. Mayne and J. Mayne

MEDICAL VOCABULARY: being an Explanation of all Names and Phrases used in the various departments of Medical Science and Practice, giving their Derivation, Meaning, Application, and Pronunciation. Sixth Edition . . Crown 8vo. [*In the Press.*]

"We have referred to this work hundreds of times, and have always obtained the information we required . . . Chemical, Botanical, and Pharmaceutical Terms are to be found on almost every page."—*Chemist and Druggist.*

THE following CATALOGUES issued by J. & A. CHURCHILL will be forwarded post free on application:

A. *J. & A. Churchill's General List of about* 650 *works on Medicine, Surgery, Midwifery, Materia Medica, Hygiene, Anatomy, Physiology, Chemistry, &c., &c., with a complete Index to their Titles for easy reference. N.B. This List includes* B, C, *and* D.

B. *Selection from J. & A. Churchill's General List, comprising all recent works published by them on the Art and Science of Medicine.*

C. *J. & A. Churchill's Catalogue of Text Books specially arranged for Students.*

D. *A Selected and Descriptive List of J. & A. Churchill's works on Chemistry, Materia Medica, Pharmacy, Botany, Photography, Zoology, The Microscope, and other branches of Science.*

E. *The Medical Intelligencer, being a List of New Works and New Editions published by J. & A. Churchill.*

[Sent yearly to every Medical Practitioner in the United Kingdom whose name and address can be ascertained. A large number are also sent to the United States of America, Continental Europe, India, and the Colonies.]

* * *

AMERICA.—*J. & A. Churchill being in constant communication with various publishing houses in Boston, New York, and Philadelphia, are able, notwithstanding the absence of international copyright, to conduct negotiations favourable to English Authors.*

LONDON: 11, NEW BURLINGTON STREET.